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# TEMPERATURE AND PRESSURE COMPONENTS
# OF SHOCK-INDUCED CHANGES IN THE
# ELECTRONIC SPECTRUM OF CARBON DISULFIDE

By

Richard H. Granholm

A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

WASHINGTON STATE UNIVERSITY
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Liquid carbon disulfide has its first electronic transition centered at 3200Å. Shock-compression of $CS_2$ up to about 80 kilobars has been shown to shift the red edge of this absorption band more than 1600Å towards longer wavelengths. In this work the conditions of temperature and pressure behind the shock wave are controlled to allow their separate effects on the $CS_2$ spectrum to be determined. The shift of the band edge appears to be a function only of temperature and pressure. Orig. ... inclu...

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# ABSTRACT

## TEMPERATURE AND PRESSURE COMPONENTS
## OF SHOCK-INDUCED CHANGES IN THE
## ELECTRONIC SPECTRUM OF CARBON DISULFIDE

by Richard H. Granholm, M.S.
Washington State University, August 1985

Chairman: G. E. Duvall

Liquid carbon disulfide has its first electronic transition centered at 3200Å. Shock-compression of $CS_2$ up to about 80 kilobars has been shown to shift the red edge of this absorption band more than 1600Å towards longer wavelengths. In this work the conditions of temperature and pressure behind the shock wave are controlled to allow their separate effects on the $CS_2$ spectrum to be determined. The shift of the band edge appears to be a function only of temperature and pressure.

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# SECTION 1

# INTRODUCTION AND SUMMARY

## 1.1 INTRODUCTION

It has been known since 1981 that liquid $CS_2$ exhibits a dramatic shift in the red edge of its 3200Å absorption band when subjected to shock-wave compression.[1]

Perhaps the earliest chemical reaction initiated by shock waves was the formation of organic molecules in the origin of life on Earth.[2] More recently, interest in the chemical effects of shock waves has been fueled by reports from Russian scientists on unusual products recovered from shocked materials,[3,4,5] and by technical advances in this country on dynamic measurements in the time scale of shock experiments. These new techniques make it possible to study the early steps in shock-induced reactions.

Bridgman first reported a reaction in liquid $CS_2$ when it is compressed statically to >45 kbar (1 kbar = 987 atm.) and 175°C.[6] Later work suggested the formation of a carbon-sulfur polymer from $CS_2$ under similar conditions.[7,8] With velocity measurements, Dick found a transition to a higher density state in $CS_2$ occurring in shock experiments at about 60 kbar.[9,10] Sheffield[11] studied the kinetics of this shock-induced transition, and found an induction period preceding relaxation to the new state, which suggested a multistep mechanism.

The first spectral measurements on $CS_2$ at high pressures were made by Ogilvie and Duvall.[1] Their first experiments showed total extinction of light transmitted through a bandpass from 2670 to 2840Å between two absorption regions in the $CS_2$ spectrum (see figure 1). The shock pressures ranged from 83 to 127 kbar. They later found that a shock of about 5-10 kbar was sufficient for extinction of this bandpass; but more significantly, the extinction occurred by apparent shifting or broadening, with pressure, of the lower wavelength absorption band towards the red. The 3200Å absorption band also expanded towards the red with increasing pressure.

The goals of the present work are to measure this shock-induced shift in the $CS_2$ absorption spectrum, and to sort out the effect of temperature from that of pressure. These goals were met by devising experiments in which the sample temperature behind
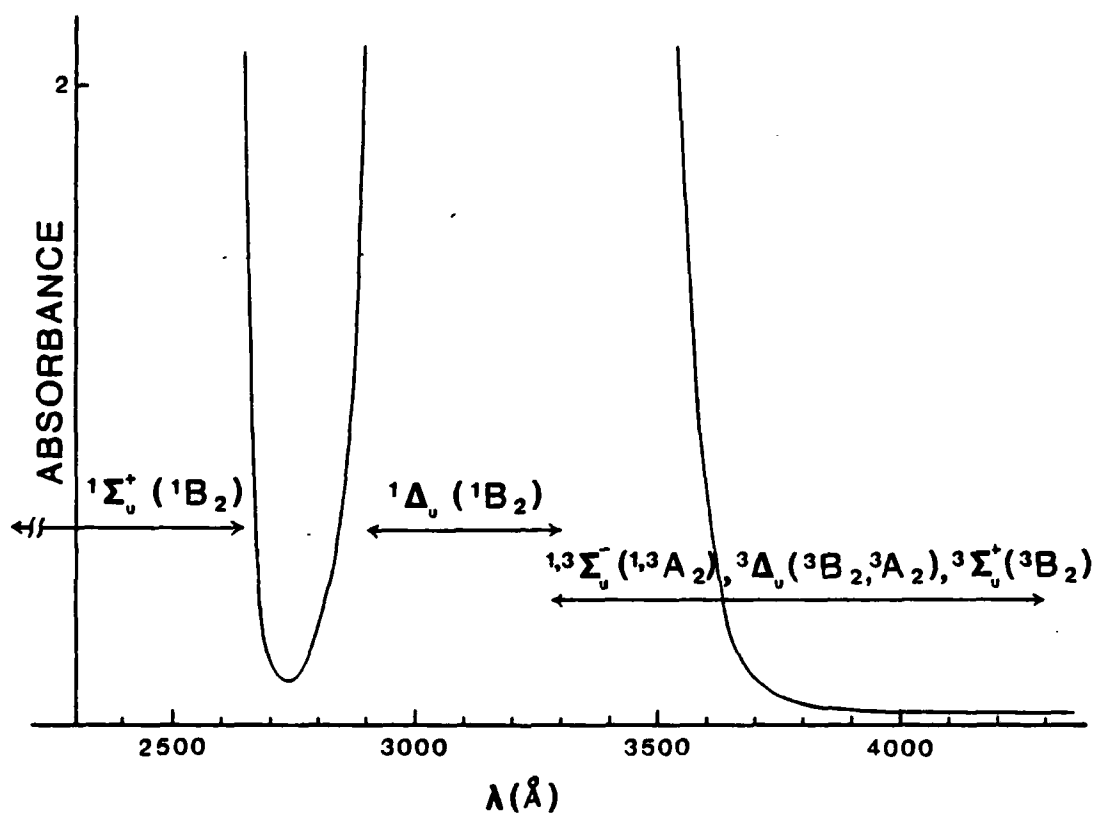
**Figure 1: Normal Spectrum of Liquid CS$_2$**

This spectrum is of a 100 micron thick sample of CS$_2$ at ambient temperature and pressure. The absorption band assignments are from references 12 and 13. The assignment of the 3300–4300Å region is uncertain.

the shock wave can be modified, thus allowing the wavelength-P-T surface for $CS_2$ to be mapped out. This mapping, i.e., the results of the experiments in this report, is shown in figure 2.

The present work deals only with "unreacted" $CS_2$, that is, with changes that occur prior to reaching the temperature and pressure threshold of the transition observed by Dick and by Sheffield.

## 1.2 SUMMARY

Liquid Carbon Disulfide exhibits a dramatic shift in the red edge of its 3200Å absorption band when compressed by shock waves. In the present work this shift was studied at various temperatures and pressures from 201°K to ~750°K and from 1 atmosphere to ~90 kilobars. These conditions were reached in shock experiments with heated and cooled spectroscopy cells, so that the $CS_2$ spectrum could be observed at a given pressure with different temperatures, or at a given temperature with different pressures. From analysis of these experiments, the spectral shift appears to be a function only of temperature and pressure. These two factors appear to be independent. $\partial\lambda/\partial T$ -vs- T is approximately linear, but $\partial\lambda/\partial P$ shows no clear dependence on either temperature or pressure, but appears to remain constant within ~± 20%.

**Figure 2: P-T-λ Surface For Liquid CS$_2$**

This surface shows the position of the red edge of the 3200Å absorption band in CS$_2$, as a function of pressure and temperature. The three curves depicting the surface are the results of shock experiments on CS$_2$ at three different initial temperatures: 201°$K$, 293°$K$, and 398°$K$. The dotted lines connect points of constant pressure.

# SECTION 2

# HARDWARE

## 2.1 MAIN FACILITY

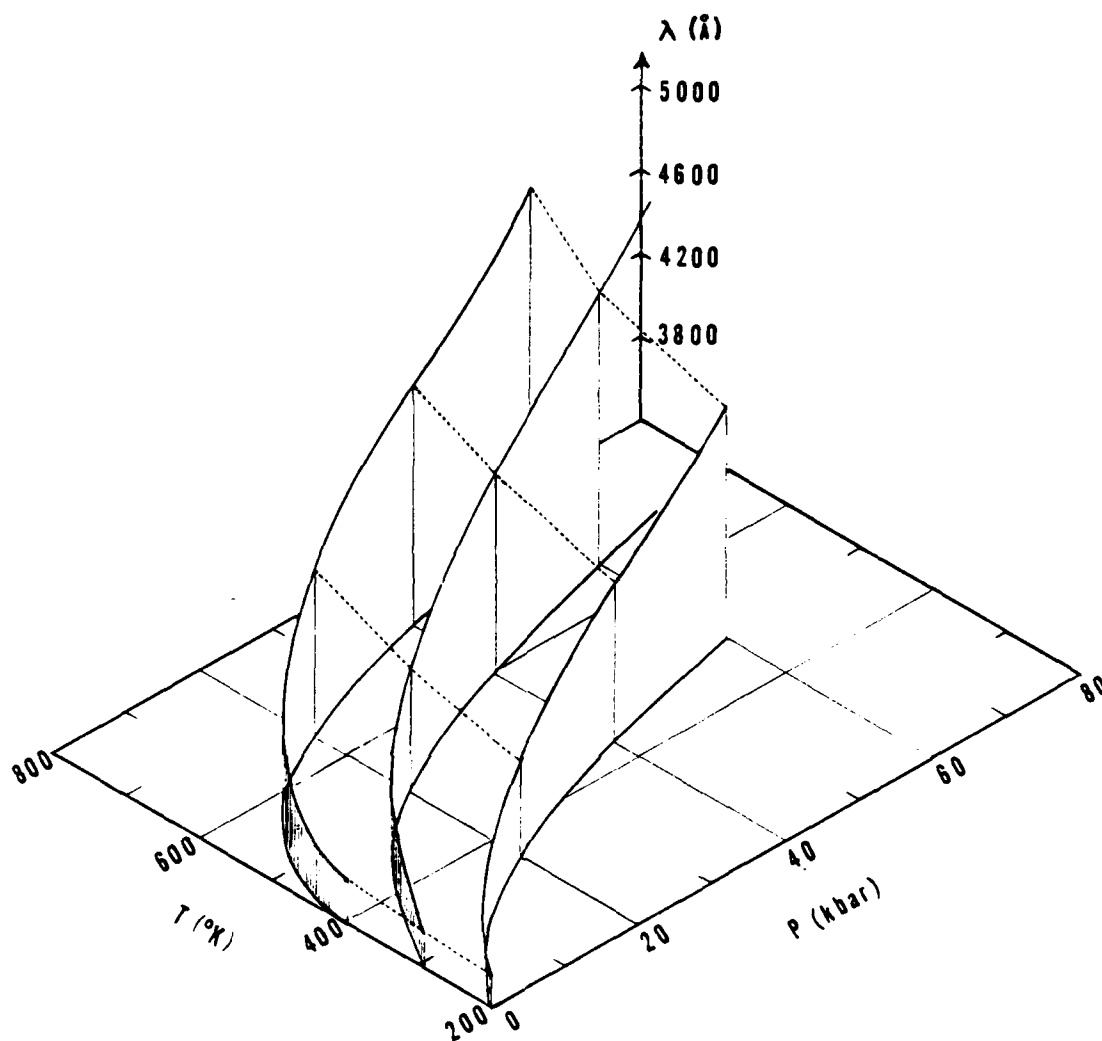The experiments were conducted with the 4 inch gas gun at the Shock Dynamics Laboratory, Washington State University. The gun is 46 feet long and has a compressed-gas breech useable to 6000 psi. Velocities up to about 1.2 km/sec can be attained with a 1 kilogram projectile. The target chamber contains optical and electrical ports for recording the experiments, and a rag-filled catcher tank, contained within a concrete bunker. A detailed description of this facility can be found in reference 14.

A gas gun is well suited for high-pressure research since it can generate a planar shock wave that is well-characterized, allowing the pressure history of a sample to be accurately measured or calculated.

## 2.2 SPECTROSCOPIC APPARATUS

A block diagram of a spectroscopy experiment is shown in figure 3. The spectrograph-streak camera consists of a Beckman & Whitley model 1500 grating dispersion unit and model 339B continuous writing streak camera using 35mm film. A diagram of the recording system is shown in figure 4. A detailed description can be found in reference 15.

Figure 5 shows a sketch of the spectroscopy cell target assembly and a projectile. Sapphire is used as the window material because it remains transparent at the pressures reached in these experiments. The impactor and back window are one inch in diameter and ~1/2 inch thick. The front window is 1 and 1/4 inches in diameter and typically 1/8 inch thick. The sample layer is typically 150 microns thick. The cell is filled through 1/16 inch copper tubes. The light source is a xenon flashlamp which is mounted on the face of the target and is flashed when a trigger pin on the target is shorted by the projectile. The entire assembly at the moment of impact is shown in cross section in figure 6. Projectile and target design are by Paul Bellamy[16].

Alignment of the target and projectile is done with a Keuffel & Esser alignment telescope. The front window of the cell is aligned parallel to the target face to within 0.5 milliradian.
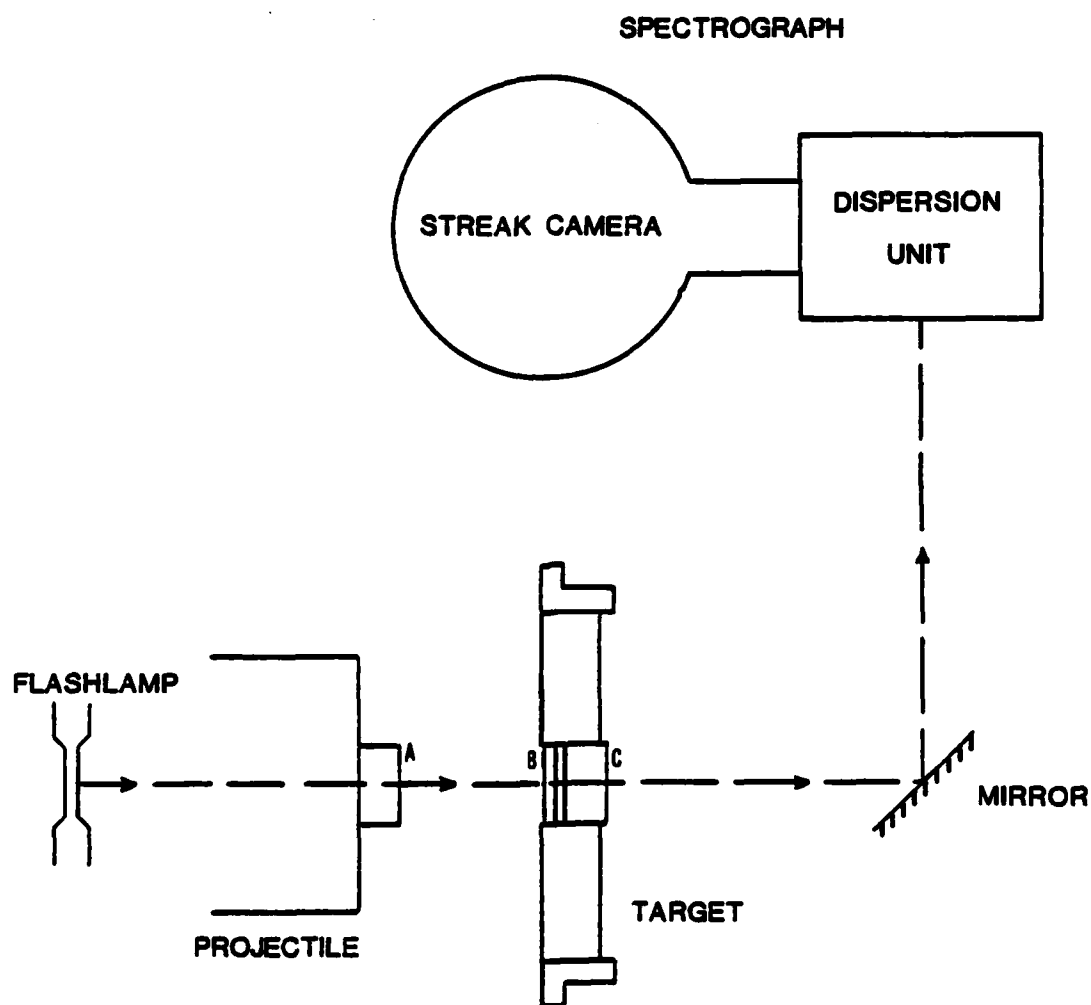
**Figure 3: Outline Of A Spectroscopy Experiment**
The xenon flashlamp is triggered just prior to impact. The light passes through the sapphire impactor, A, then through the sample cell mounted in the target. B and C are the front and back sapphire windows of the sample cell. The light is then directed to a spectrograph where a time-resolved spectrum is recorded as the sample is compressed by the shock wave.
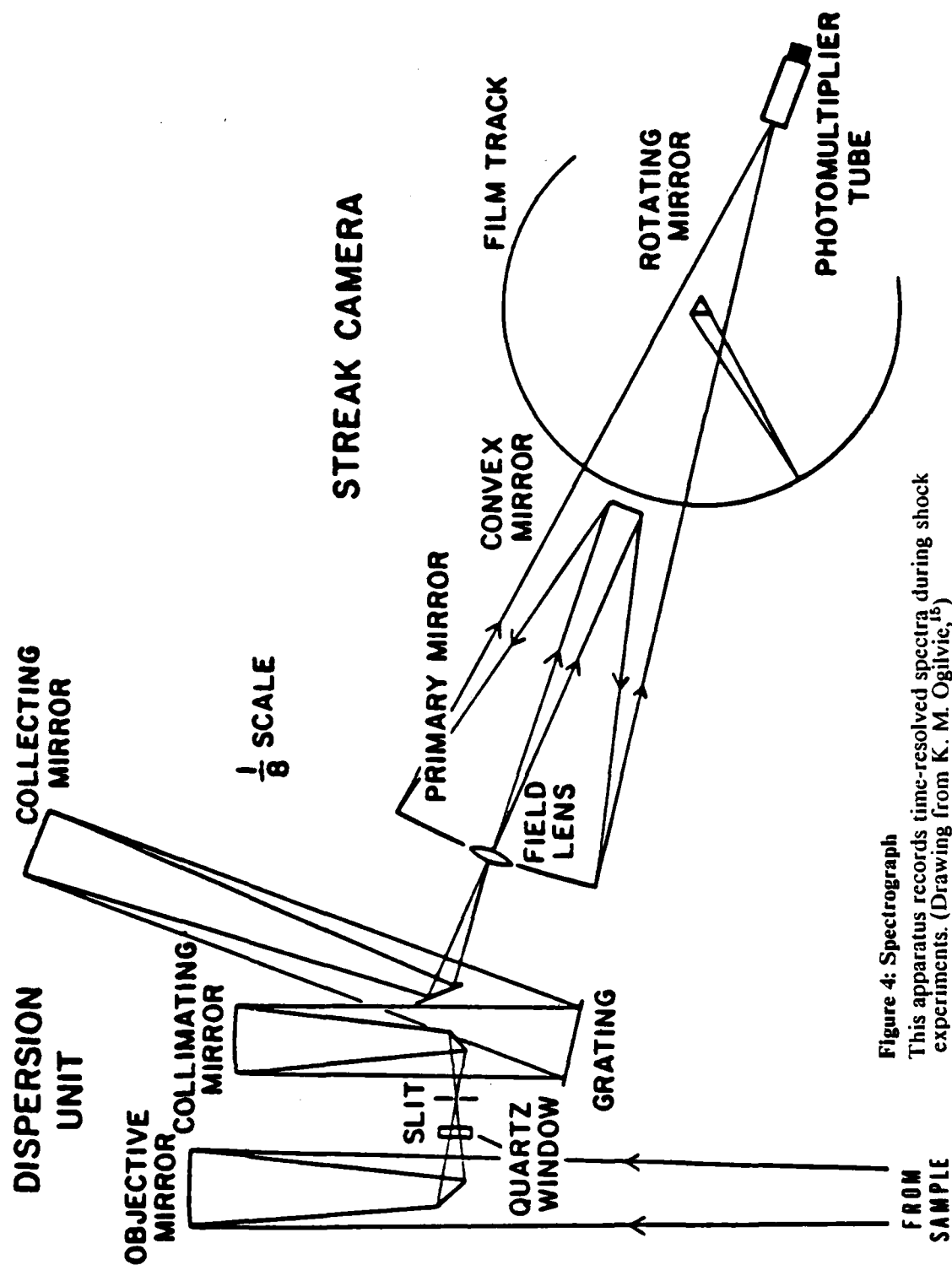
**Figure 4: Spectrograph**
This apparatus records time-resolved spectra during shock experiments. (Drawing from K. M. Ogilvie,[16])

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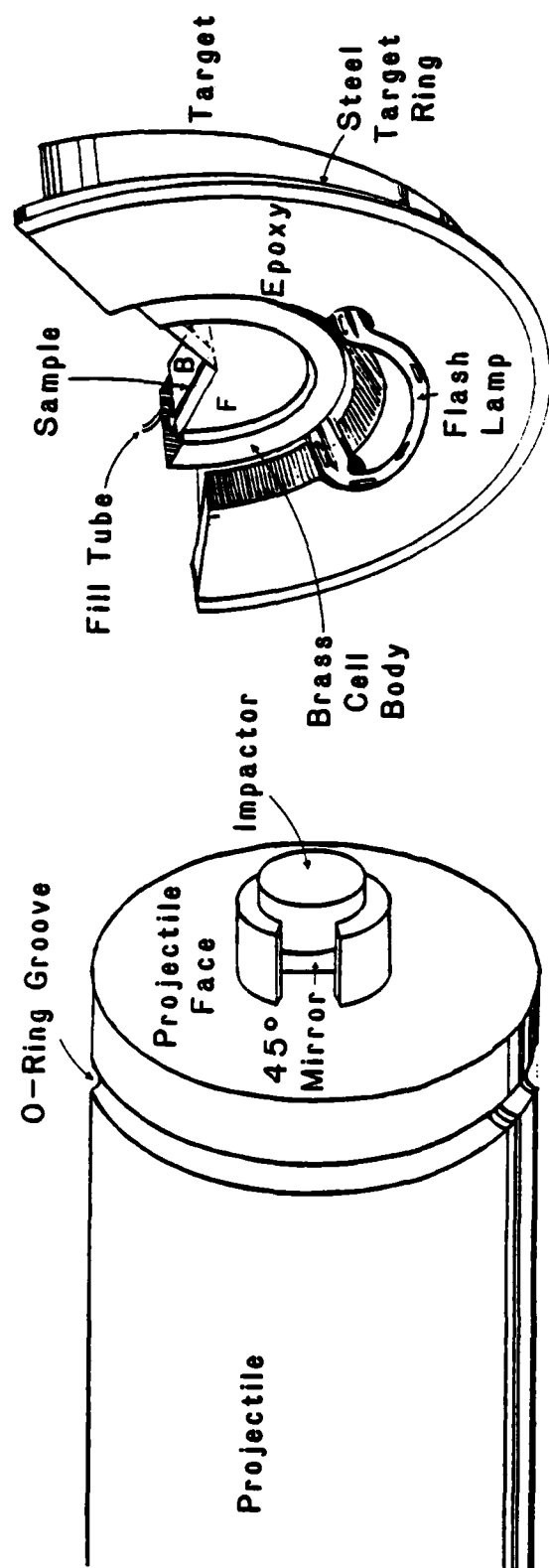


**Figure 5: Projectile And Target Assembly For Spectroscopy Experiments**
F) sapphire front window; B) sapphire back window. (Drawing by S. Arione.)

10

RETAINING RING

O-RINGS

BRASS CELL BODY

SUPPORT FIN

ALIGNMENT SCREW

SUPPORT TUBE

SAPPHIRE ANVIL

LIQUID CAVITY

SAPPHIRE FRONT WINDOW

EPOXY FILLER

TARGET RING

FLASH LAMP

PROJECTILE

TURNING MIRROR

SAPPHIRE IMPACTOR

TURNING MIRROR

Figure 6: Projectile And Target Assembly At Impact
(Design and drawing by P. Bellamy.)

## SECTION 3

## DESCRIPTION OF EXPERIMENTS

### 3.1 SHOCK-COMPRESSION OF $CS_2$ : STEPWISE LOADING (SWL)

When the impactor strikes the front window of the spectroscopy cell, a shock wave is propagated forward into the window (and a backward-facing wave propagates into the impactor), causing a sudden jump in pressure and temperature. When this wave enters the liquid, its amplitude is reduced because of the lower shock impedance of the liquid compared to sapphire, but when the wave reaches the rear window it is reflected, causing a second jump in pressure and temperature. In this way, the pressure in the liquid "rings up" through a series of reflections until it reaches the initial sapphire-sapphire impact pressure. This process, which we shall call stepwise loading (SWL), is illustrated in pressure - particle-velocity space in figure 7.

The normal spectrum of liquid $CS_2$ is shown in figure 1, and a time-resolved spectrum of $CS_2$ in a shock experiment is shown in plate 3. Xenon lines are visible on the left in plate 3, until the gas in the flashlamp becomes hot enough for broad band emission. The 3200Å absorption band appears at the bottom of the record, with its upper edge at 3550Å. At impact there is a slight increase in total transmitted light when the reflective surfaces of impactor and cell window are merged. 280 nanoseconds later the shock enters the $CS_2$ causing a sudden jump to 8.5 kbar and 428°$K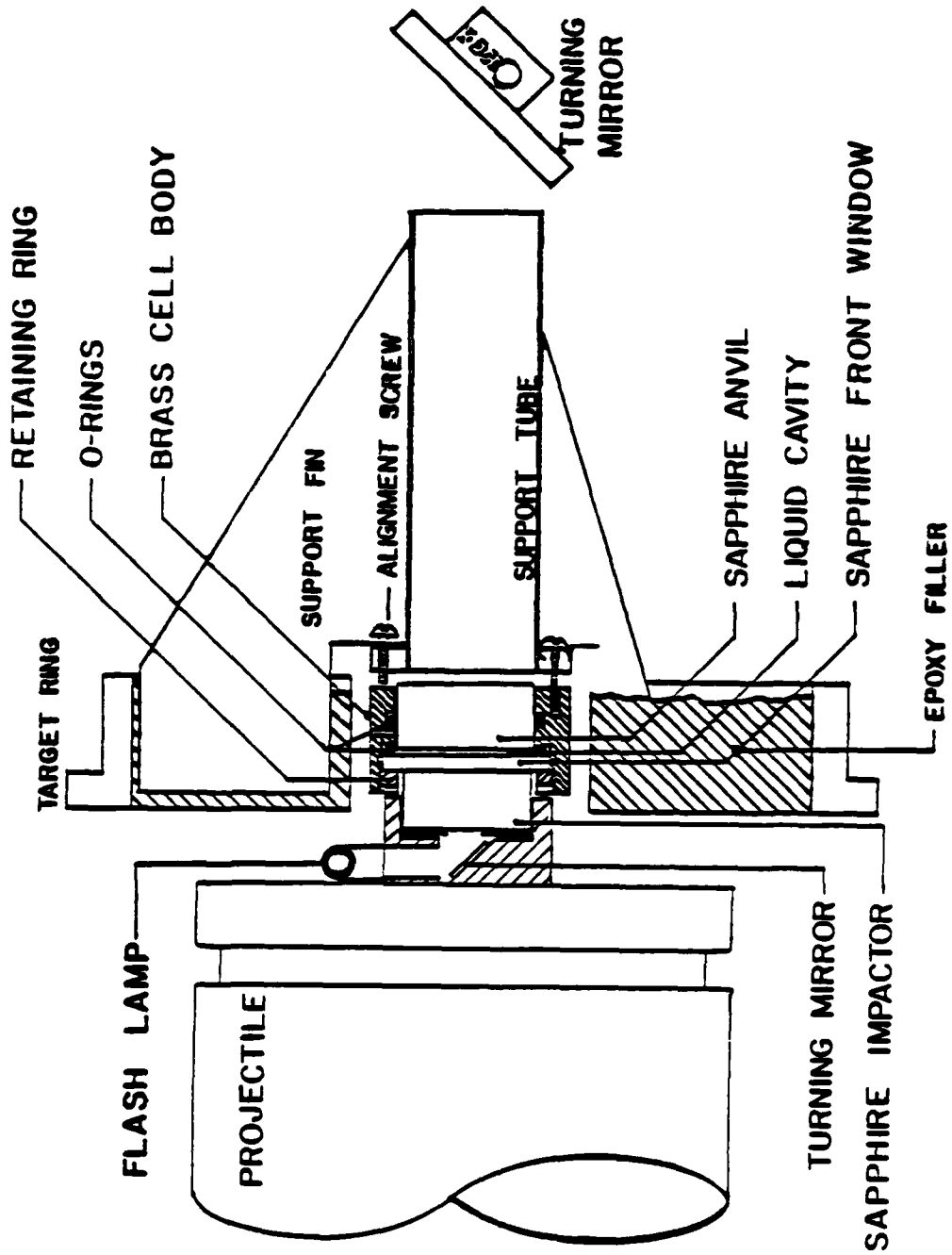$. Simultaneously the edge of the absorption band shifts about 200Å to the red. The shock wave traverses the layer of $CS_2$ (typically 150 microns) in ~85ns at which point it is reflected back into the $CS_2$ causing another jump in temperature and pressure and another shift of the band edge. The first three or four such steps are visible in this record. When the final values are reached, 81 kbar and 700°$K$ , the band edge levels off at ~5300Å.

Pressure and temperature are difficult to measure directly in shock experiments so these values are calculated for each step from an equation of state (see section 4). Even after the steps become too small to be seen on the record, their location in time is known from the known values of shock velocity in $CS_2$. Thus one experiment can give 10 or 12 points on a curve of wavelength -vs- pressure. The Pressure history of the sample in a

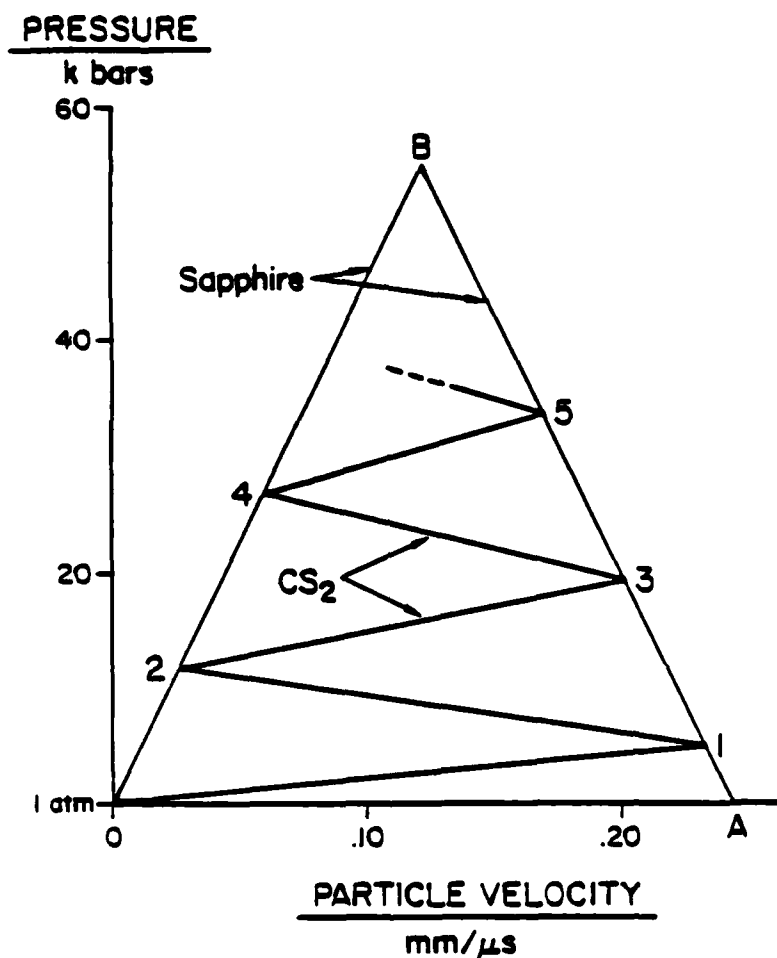**Figure 7: Stepwise Loading**

The shocking up process in a $CS_2$ layer between sapphire plates. The slope of each curve is a characteristic of the material (sapphire or $CS_2$). Point A is the initial projectile velocity, and 0 is the initial target condition. Point B represents the conditions of the initial sapphire on sapphire impact. The reverberating shocks take the $CS_2$ to states 1, 2, 3, etc.

typical experiment is graphed in figure 8. Alignment of target and projectile is critical in these experiments since tilt would introduce error in the calculated position in time of the shock wave, by "smearing out" the stepwise jumps in pressure, temperature, and wavelength.


### 3.1.1 ROOM TEMPERATURE SWL EXPERIMENTS

In all the shock experiments described in this report, the original experimental record is a strip of 35mm film with the $CS_2$ spectrum dispersed in wavelength ($\lambda$) across the film and in time along the film, as seen in plates 1 through 7. The first step in analysis is digitizing the position of the 3200 Å band edge. This is accomplished on a Gaertner measuring microscope interfaced to an Apple computer for recording the data. A fortran program is run separately to simulate the experiment. This program is called SHOCKUP and was originally written by Kendal Ogilvie[15] to calculate pressure, temperature, and time, using the Sheffield-Duvall equation of state (see section 4) and the shock jump conditions, as the $CS_2$ "shocks up" in a SWL experiment. The program currently in use was written by Robin Collins.[17]

The original data give $\lambda$ -vs- time and SHOCKUP gives P -vs- time. By matching the time in the experiment to the time calculated with the program, we obtain $\Delta\lambda$ -vs- P, where $\Delta\lambda$ is the shift of the band edge relative to its original position. The original shot record of plate 3 is shown in digitized form in figure 9. The times of each stepwise jump in $\lambda$ are readily matched with SHOCKUP times, which are plotted on the same graph.

Five room-temperature experiments were performed, i.e., the $CS_2$ samples were initially at $\sim 20^\circ C$. The impact pressures ranged from 54 to 130 kbars. (One of these experiments, shot 82-015, was performed by Paul Bellamy; the rest were by this author.) Copies of the original shot records are shown in plates 1 through 5. The $\Delta\lambda$ -vs- P data from all five experiments are plotted in figure 10, and are fit quite well by the cubic equation:

$$\Delta\lambda = 26.75P - 0.2554P^2 + 0.002252P^3 \qquad (\Delta\lambda \ in \ Å; \ P \ in \ kbar)$$

as shown by the solid line in the figure. The T-P profile, calculated with SHOCKUP, for
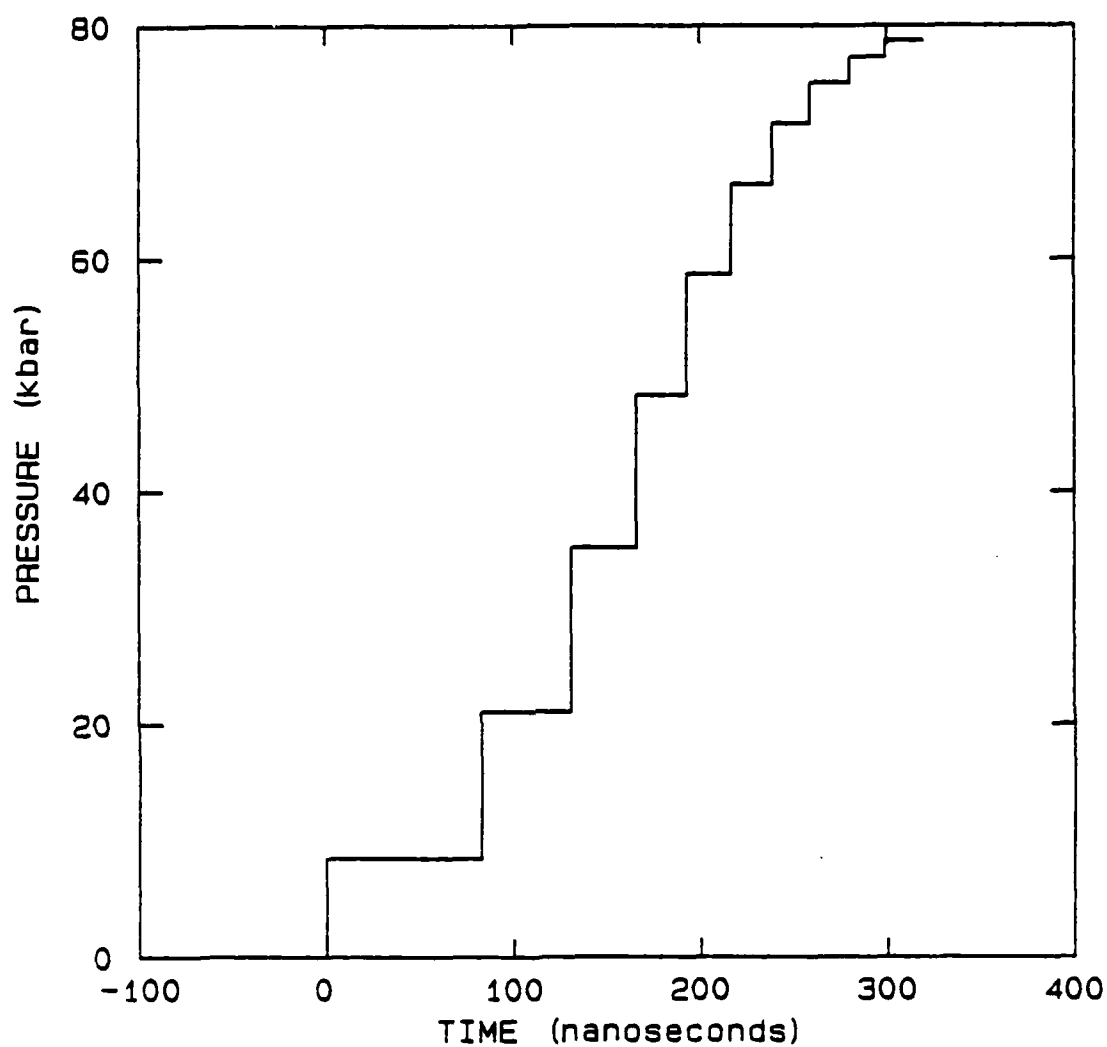
**Figure 8: Pressure History Of $CS_2$ In A Typical Experiment**

This shows the pressure, just behind the reverberating shock wave, of a 160 micron thick sample of $CS_2$ in a stepwise loading experiment. The shock just enters the liquid at time = 0. Impact pressure is 81 kilobars.
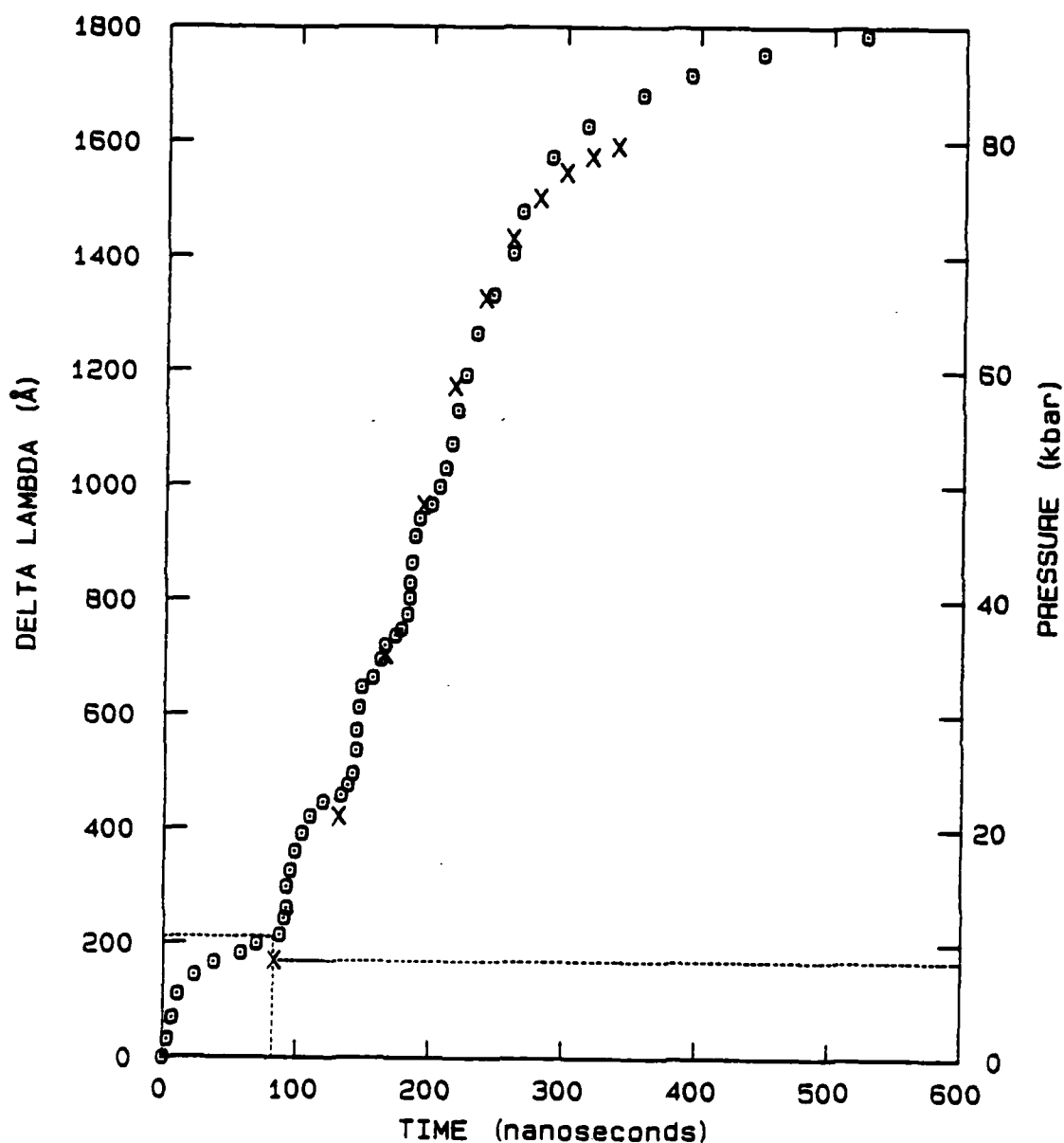
**Figure 9:** Shot 82-037; $T_0 = 20°C$ ($293°K$)

⊙ - $\Delta\lambda$ -vs- time; digitized band edge from original shot record.

X - Pressure -vs- time; calculated by SHOCKUP.

At time = 0, the shock just enters the $CS_2$. At the first X, the shock completes one transit of the $CS_2$ and is just about to reflect from the back sapphire window. At this instant the $CS_2$ pressure is homogeneous throughout the cell. The dotted line shows how pressure, calculated by SHOCKUP, is correlated with the wavelength shift of the band edge.
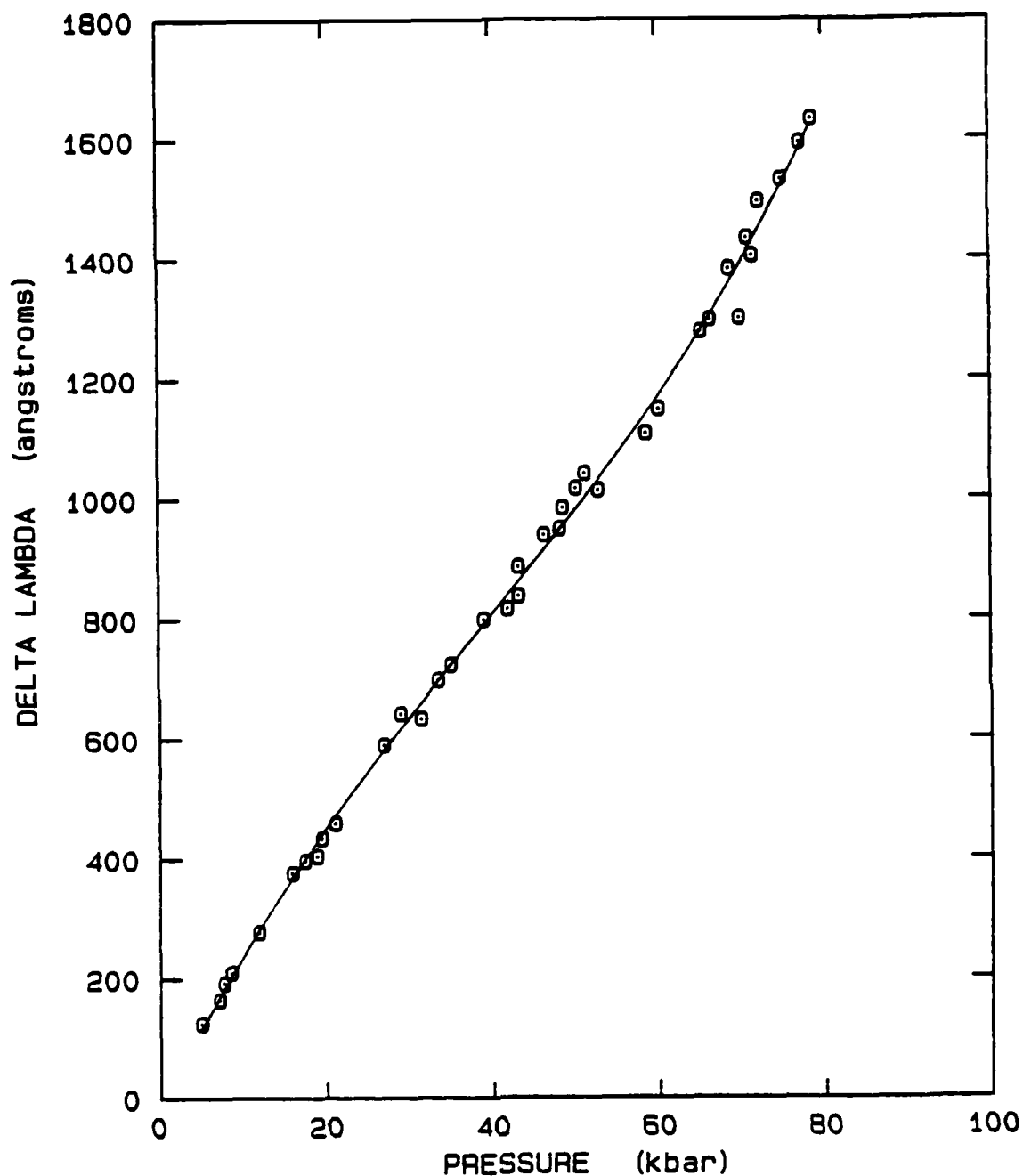
**Figure 10:** $\Delta\lambda$ -vs- P For Room Temperature SWL Experiments ($T_0 = 20°C$)

The circles show the position of the 3200Å $CS_2$ band edge for each pressure step in the five shock experiments recorded in plates 1-5. The solid line is a least squares fit of the data. The equation of the line is:

$$\Delta\lambda = 26.75P - 0.2554P^2 + 0.002252P^3$$

$\Delta\lambda$ is in angstroms and P is in kilobars.
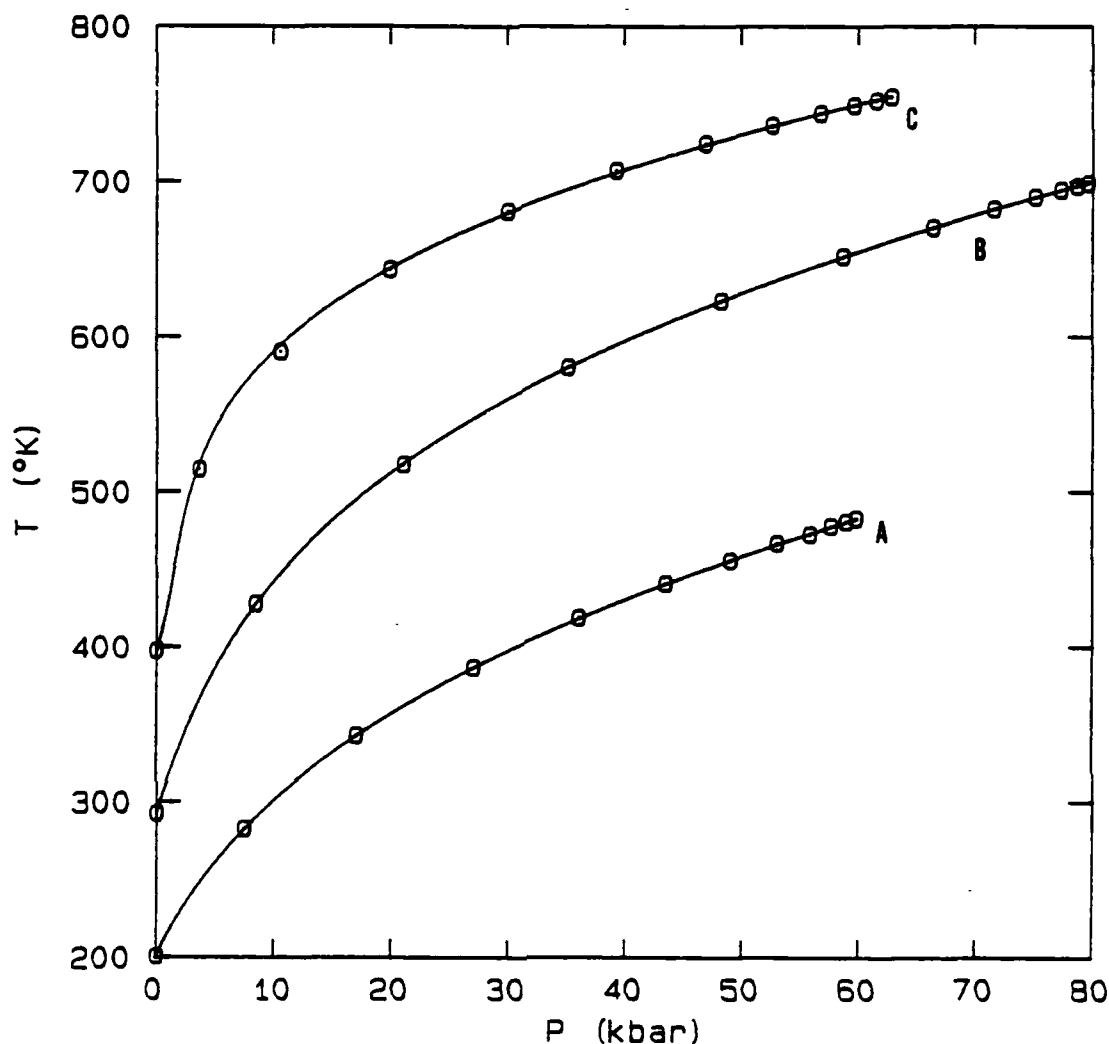
**Figure 11: T-P Profiles Calculated By SHOCKUP**

Curve A) cooled cell experiment, $T_0 = 201°K$; curve B) room temperature experiments, $T_0 = 293°K$; curve C) heated cell experiment, $T_0 = 398°K$. The circles are the actual SHOCKUP data; the solid lines are cubic fits to the data. The equations for the (inverse) lines are as follows:

A)  $P = -8.075 + 5.358 \times 10^{-2} T - 2.429 \times 10^{-4} T^2 + 8.765 \times 10^{-7} T^3$

B)  $P = -32.94 + 2.544 \times 10^{-1} T - 7.378 \times 10^{-4} T^2 + 8.640 \times 10^{-7} T^3$

C)  $P = -185.6 + 1.200 T - 2.611 \times 10^{-3} T^2 + 1.930 \times 10^{-6} T^3$

where P is in kilobars and T is in Kelvins. The equations are valid for the intervals plotted.

this room-temperature SWL curve is graphed as curve B in figure 11.

### 3.1.2 HEATED CELL

In order to reach higher temperatures behind the shock, the initial temperature of the $CS_2$ sample was raised from room temperature to 125°C. A heated spectroscopy cell was devised for this experiment and is shown in figure 12. A heating-coil groove was cut around the circumference of the brass body of a standard cell, and a 0.1 inch o.d. coil of 28 gauge nichrome wire was cemented in the groove with Sauereisen P-1 refractory cement. This heater had a resistance of 21 ohms and was powered with 15 - 20 volts AC from a variable transformer. Pre-shot temperature was measured via a thermocouple pressed against the cell body with a screw. A washer-shaped brass retainer was fastened over the back window to keep the press-fit sapphire from being pushed out by the 100psia vapor pressure of $CS_2$ at 125°C.[18] In an alignment test at 125°C, the filled cell remained parallel to the target ring face to within 0.7 milliradian. This value did not change after two cycles of heating and cooling. (Fresh $CS_2$ was used in the actual shock experiment.)

A copy of the original record of the heated cell experiment is shown in plate 6. The impact pressure was 65 kbar and the cell thickness was 164 microns. The digitized band edge from the original record is graphed in figure 13 along with the pressure-time calculations from SHOCKUP. $\Delta\lambda$ -vs- P taken from this figure is plotted as curve h in figure 14. The T-P profile for this experiment is plotted as curve C in figure 11.

### 3.1.3 COOLED CELL

A standard spectroscopy cell was modified for cooling by soldering two turns of 3/16 inch copper tubing around the cell body prior to assembling the cell (figure 15). Liquid nitrogen was pumped through the tubing via a long rubber hose, allowing the $N_2$ to vaporize before reaching the cell and thus giving some measure of temperature control. Cell alignment was to 0.4 milliradian at room temperature. At −72°C alignment was difficult to measure due to frosting even inside the glove bag built around the alignment tele-

side view
cross section
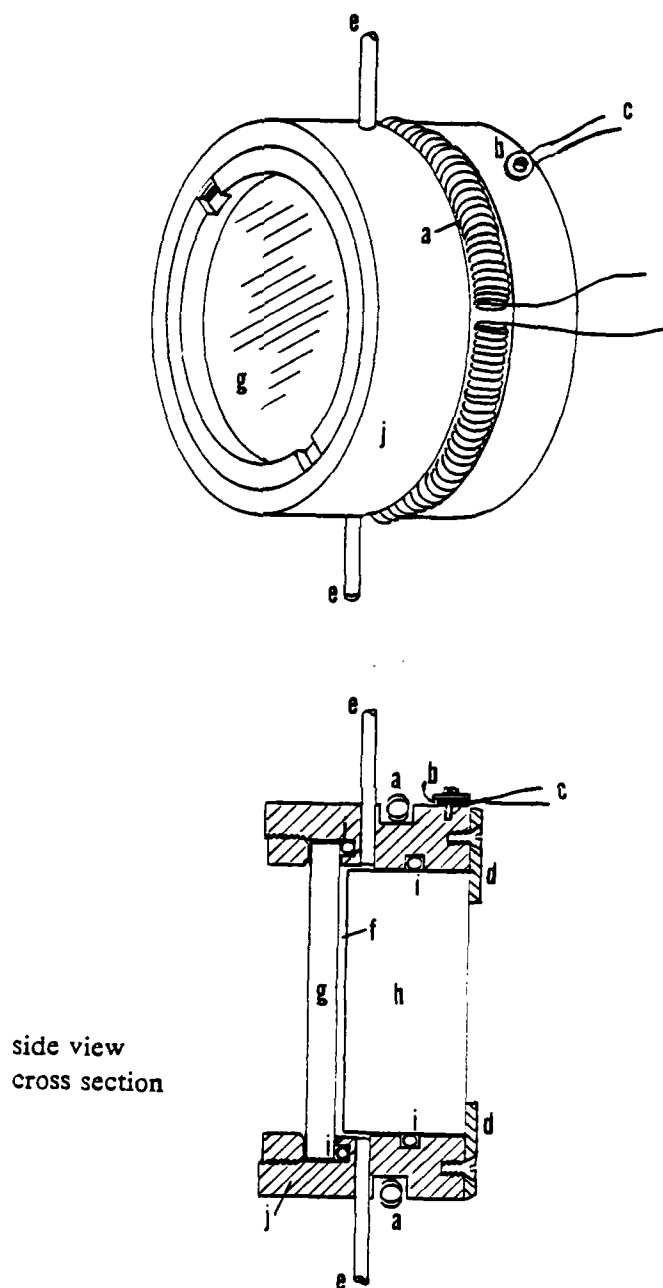
**Figure 12: Heated Spectroscopy Cell**

a) heater coil (insulating cement not shown); b) thermocouple beneath screw & washer; c) thermocouple leads; d) retaining ring; e) fill tubes; f) sample cavity; g) front sapphire window; h) back sapphire window; i) o-ring seals; j) brass cell body.
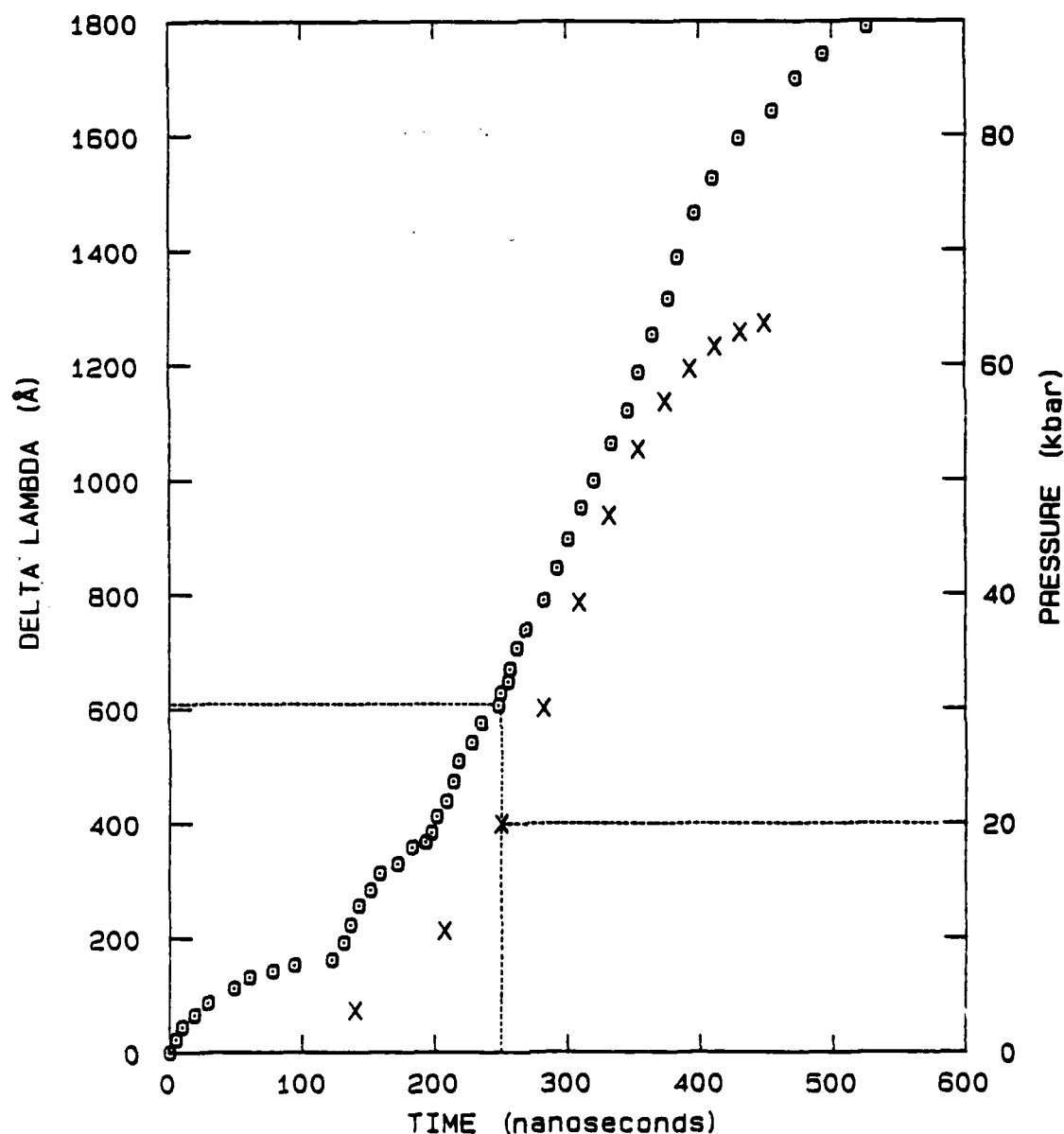
**Figure 13: Heated Cell Experiment (Shot 83-022); $T_0 = 398°K$**

⊙ - $\Delta\lambda$ -vs- time; digitized band edge from original shot record.

X - Pressure -vs- time; calculated by SHOCKUP.

At time = 0, the shock just enters the $CS_2$. At the first X, the shock completes one transit of the $CS_2$ and is just about to reflect from the back sapphire window. At this instant the $CS_2$ pressure is homogeneous throughout the cell. The dotted line shows how pressure, calculated by SHOCKUP, is correlated with the wavelength shift of the band edge.
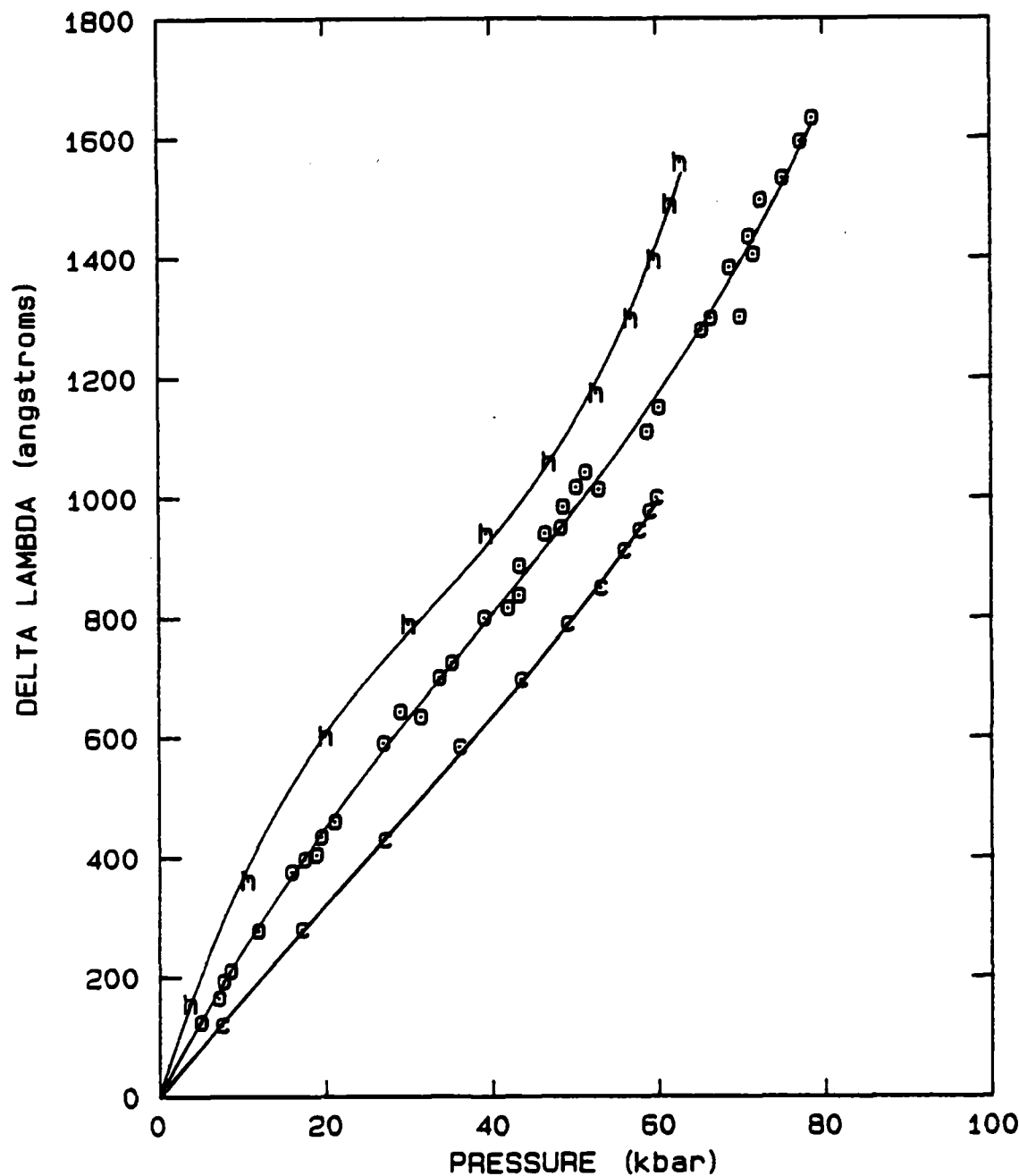
Figure 14: $\Delta\lambda$ -vs- P For The 3200Å $CS_2$ Band Edge

The solid lines are least squares cubic fits to the data. The equations of the lines are given: ⊙) data from five shock experiments with $T_0$ = 293°K, $\Delta\lambda$ = 26.75P − 0.2554P² + 2.252×10⁻³P³. ⊙) cooled cell experiment, $T_0$ = 201°K, $\Delta\lambda$ = 17.404P − 8.3074×10⁻²P² + 1.1531×10⁻³P³. h) heated cell experiment, $T_0$ = 398°K, $\Delta\lambda$ = 45.019P − 0.92222P² + 9.4615×10⁻³P³.

$\Delta\lambda$ is in angstroms, P is in kilobars.

side view
cross section
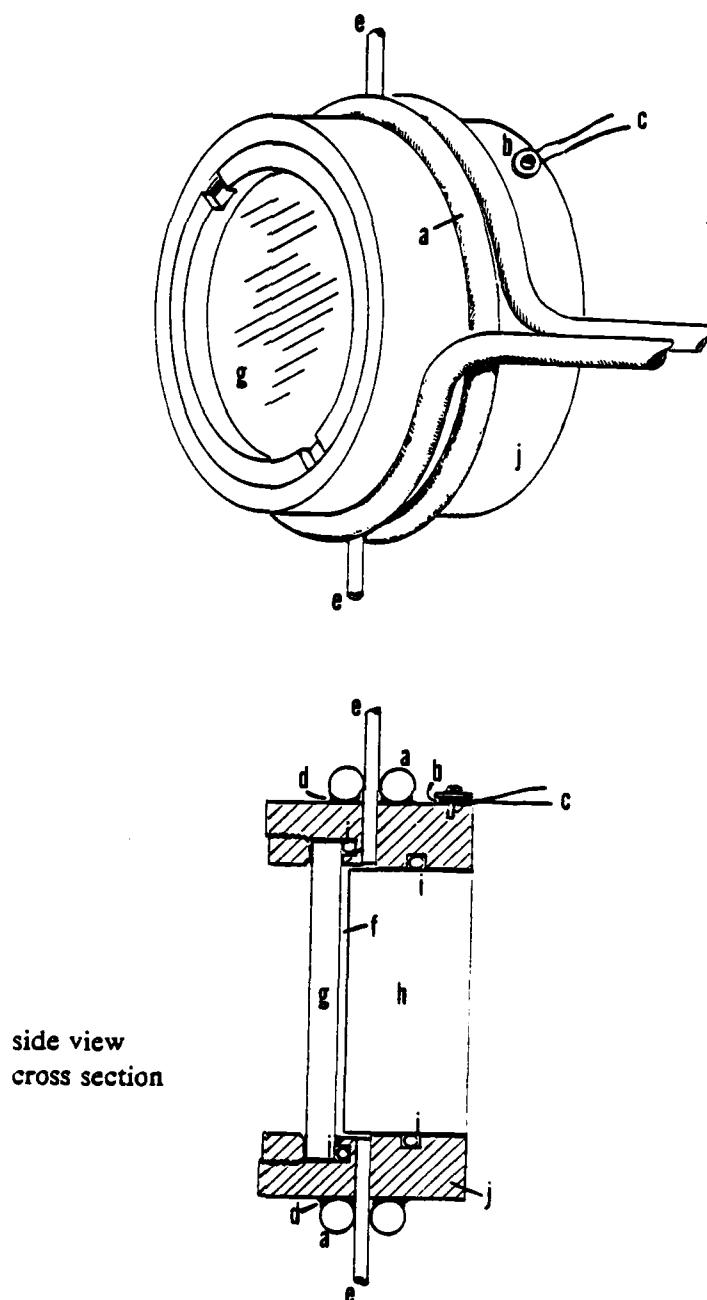
**Figure 15: Cooled Spectroscopy Cell**

a) cooling coil (3/16th-inch copper tubing); b) thermocouple beneath screw & washer; c) thermocouple leads; d) solder; e) fill tubes; f) sample cavity; g) front sapphire window; h) back sapphire window; i) o-ring seals; j) brass cell body.

scope, but maximum tilt was no greater than ~1.0 milliradian.

Plate 7 shows a copy of the original shot record for the cooled cell experiment. The initial temperature was $-72^{\circ}C$ ($201^{\circ}K$), the impact pressure was 61 kbar, and the cell thickness was 158 microns. The digitized band edge from the original record is graphed in figure 16 along with the pressure-time calculations from SHOCKUP. $\Delta\lambda$ -vs- P taken from this figure is plotted as curve C in figure 14. The T-P profile for this experiment is plotted as curve A in figure 11.

## 3.2 STATIC MEASUREMENTS

In the shock experiments, spectra are recorded during compression, but also during two or three microseconds prior to impact. Thus $CS_2$ spectra were obtained at ambient pressure and at $201^{\circ}K$, $293^{\circ}K$, and $398^{\circ}K$ (at $398^{\circ}K$ $CS_2$ vapor pressure is 6.8 atm., which is still ~zero on the scale of these experiments). See figure 17. These measurements show a band edge shift of ~29Å as T changes from 201 to $293^{\circ}K$, and ~48Å as T changes from 293 to $398^{\circ}K$. The spectra at ambient pressure of a 100 micron layer of $CS_2$ at $298^{\circ}K$ and $398^{\circ}K$ were also recorded, with a little more accuracy, on a Cary-14 spectrophotometer. In these spectra the 3200Å band had broadened to the red by 42Å (at Absorbance=2), as T changed from $298^{\circ}K$ to $398^{\circ}K$, but the blue edge moved only 6Å to the blue (figure 18).
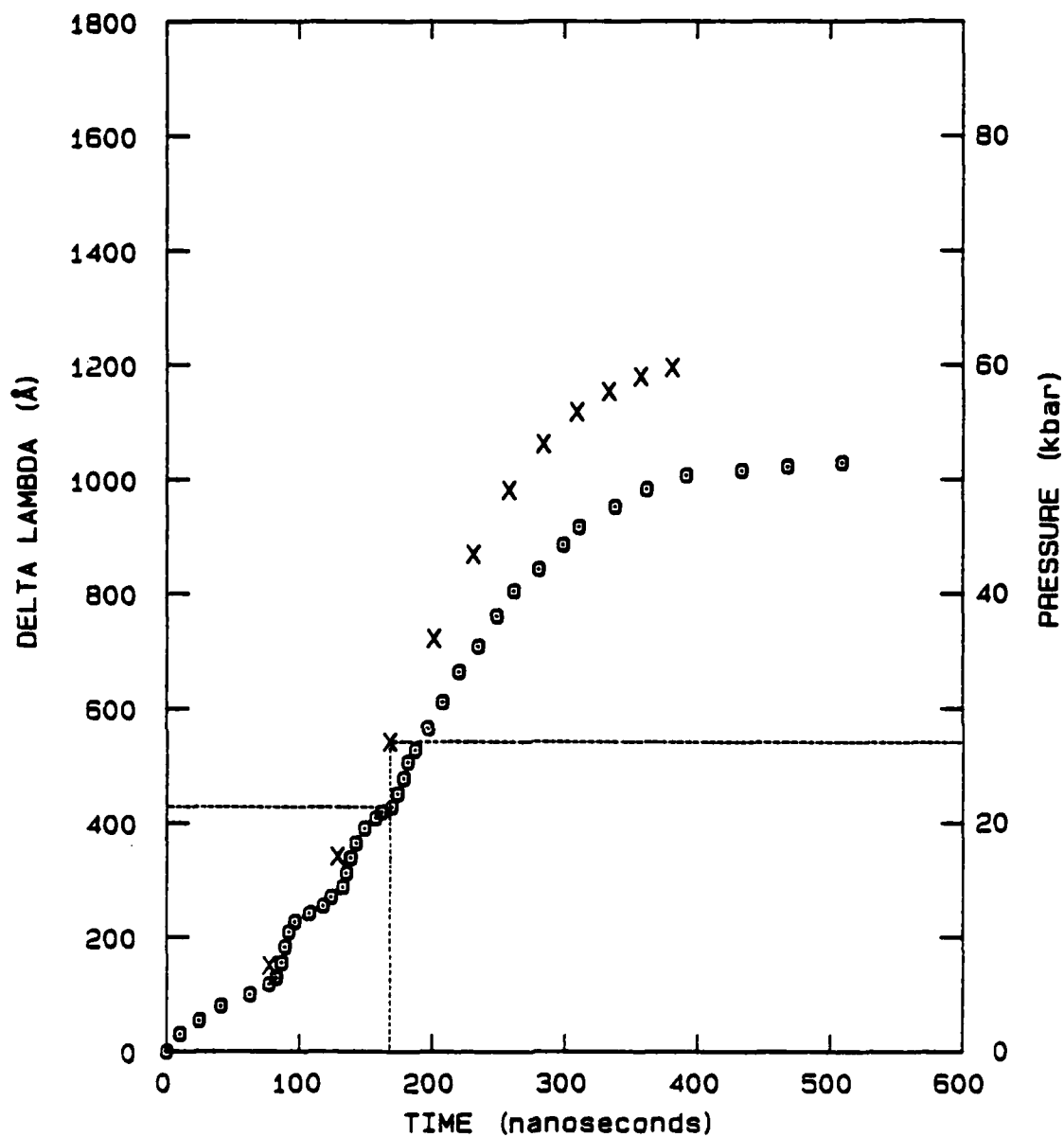
**Figure 16: Cooled Cell Experiment (Shot 83-031); $T_0 = 201°K$**

       ⊙ - $\Delta\lambda$ -vs- time; digitized band edge from original shot record.

       X - Pressure -vs- time; calculated by SHOCKUP.

At time = 0, the shock just enters the $CS_2$. At the first X, the shock completes one transit of the $CS_2$ and is just about to reflect from the back sapphire window. At this instant the $CS_2$ pressure is homogeneous throughout the cell. The dotted line shows how pressure, calculated by SHOCKUP, is correlated with the wavelength shift of the band edge.
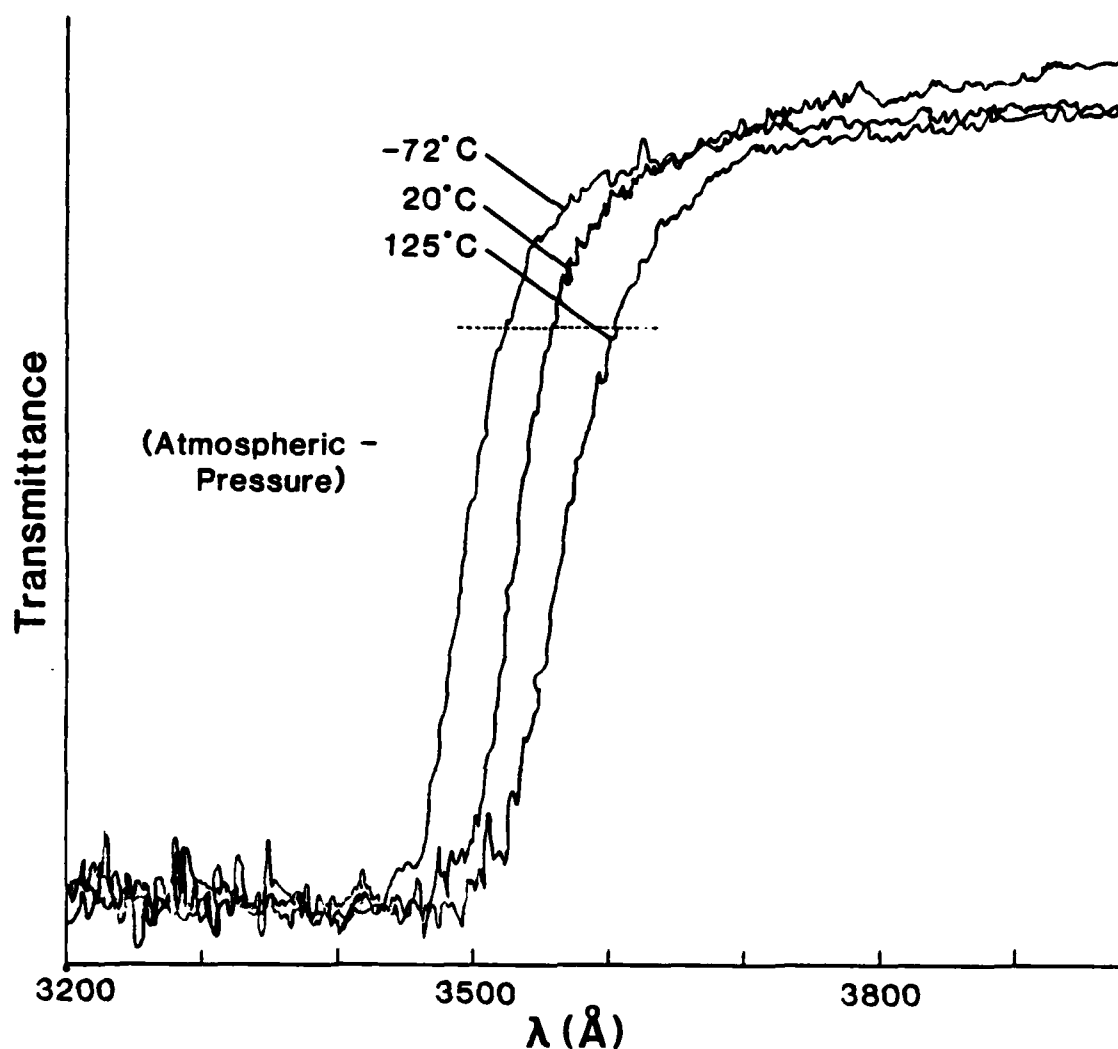
**Figure 17: CS$_2$ Spectrum Showing Red Edge Of Absorption Band**

Pre-shock CS$_2$ spectra for shots 83-031, 82-031, and 83-022, at $-72°C$ ($201°K$), $20°C$ ($293°K$), and $125°C$ ($398°K$) respectively. These spectra were obtained by densitometer scans of the original 35mm film shot records. The figure shows the band-edge shift with temperature at constant (ambient) pressure. The dotted line shows the approximate level of film density at which all the records were read. This is the level at which the band edge just becomes visible by eye.
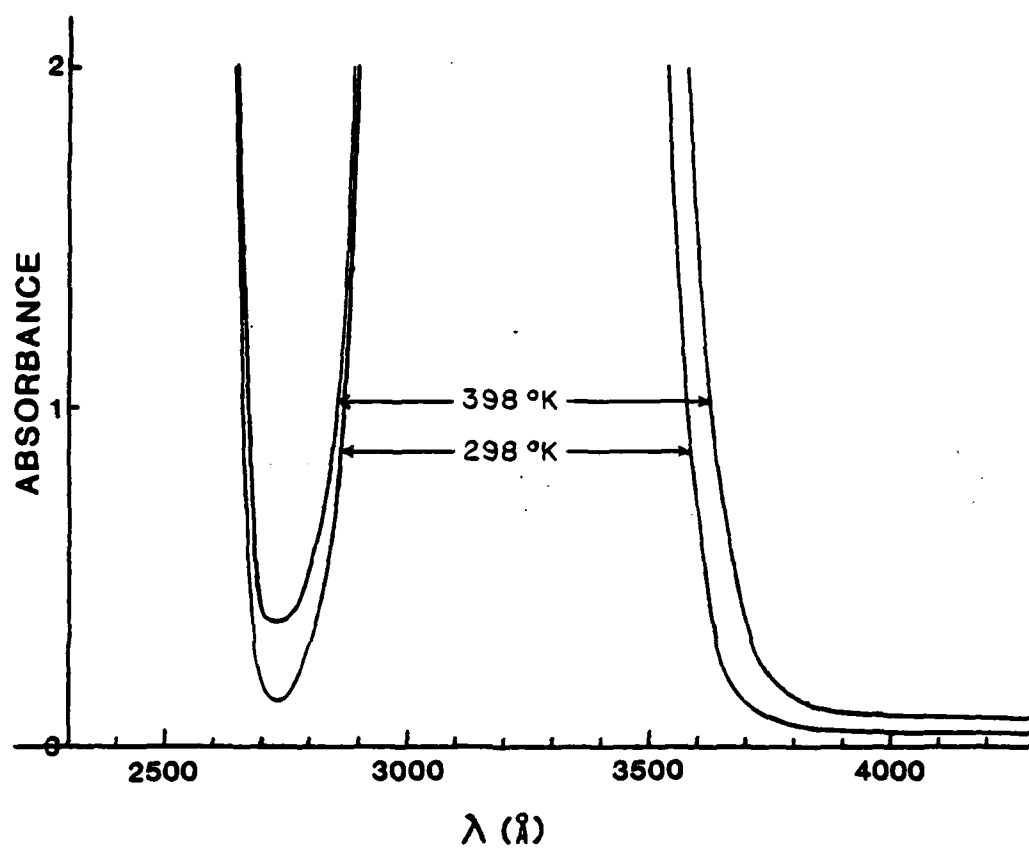
**Figure 18: Spectrum Of Liquid CS$_2$**

The spectra shown are of a 100 micron thick sample of CS$_2$ at 298°K and at 398°K, recorded at ambient pressure on a Cary 14 spectrophotometer.[2]

# SECTION 4
## $CS_2$ EQUATION OF STATE

Finding equations of state for high pressures and temperatures has been a long-standing problem. They are constructed from meager data, largely from shock measurements, which provide no temperature information. These equations are commonly modelled after standard forms, for example, Woolfolk, Cowperthwaite, and Shaw[19] have proposed an empirical "universal" liquid Hugoniot† based on shock data for several liquids. The $CS_2$ equation of state used in this report was written by Sheffield and Duvall.[20] It is based on the Woolfolk, Cowperthwaite, and Shaw model which gives an excellent fit to $CS_2$ shock data (pressure and volume), but gives no information on temperature. Sheffield's temperature calculation is based on an assumed function for $C_v$. To give an idea of the uncertainties involved, the temperature of $CS_2$ after shock-compression to 50 kbar has been calculated from three different equations of state (for step-wise loading, with impact pressure of 54 kbar):

$$\text{Sheffield-I} \text{ ----------- } 732°K$$
$$\text{Sheffield-II} \text{ ---------- } 610°K$$
$$\text{Mie-Gruneisen} \text{ ------ } 551°K‡$$

Sheffield-I was written by Steve Sheffield as part of his PhD thesis;[11] Sheffield-II is the Sheffield-Duvall equation of state used in this report. It is impossible to assess the accuracy of these calculations without furthur thermal measurements. The Sheffield-II pressure calculations have been verified by Sutherland,[21] who used a quartz gauge to measure $CS_2$ pressures up to 40 kbar in an SWL (stepwise loading) experiment. The agreement was within ~2%.

For the "cold" experiment (shot 83-031), measured values of thermodynamic state functions for $CS_2$ at −72°C were obtained from the literature and were used as initial values in the Sheffield equation of state. These quantities were V (specific volume), alpha (thermal volume expansivity), $K_T$ (isothermal bulk modulus), and $C_P$ (isobaric specific heat). The first three were measured graphically from P-V-T data compiled by P. W. Bridgman.[22] These data are from different sources so I will say more about them. The

---

† A Hugoniot is the locus of thermodynamic end-points reached by shock-compression of a material. It is a single curve on the 3-dimensional thermodynamic surface for that material.

‡ With $\Gamma/V$ constant, specific heat was allowed to vary with temperature according to the Debye theory.

most complete P-V-T measurements on $CS_2$ above $0^oC$ were made by Bridgman and published in 1913.[23] In these experiments T was varied from $0^oC$ to $80^oC$ and P was varied from 500 atm to 12000 atm (0-500 atm data were taken from Amagat, as described in Bridgman's paper). These data were extended below $0^oC$ to $-100^oC$ at pressures from 1 atm to 1000 atm by Seitz and Lechner in 1916.[24] The Seitz and Lechner data were later compiled by Bridgman with his own data and published in the International Critical Tables.[22] The value for $C_p$ at $-72^oC$ was taken from reference 25. These values are listed in table 1.

For the $125^oC$ experiment (shot 83-022), thermodynamic quantities at ambient pressure had to be extrapolated beyond known values, as no measurements could be found above $80^oC$. V and alpha were calculated from a cubic equation fit to V-T data for $CS_2$ from $-34^oC$ to $60^oC$.[26] This equation was checked against the Bridgman data and the Seitz and Lechner data and made an excellent fit from $-34^oC$ to the limit of Bridgman's data at $80^oC$. $K_T$ was calculated by plotting Bridgman's data against T, and extrapolating to $125^oC$. $C_p$ at $125^oC$ was also obtained by extrapolation,[25] but should be reliable because $C_p$ changes little with temperature. The initial values used in this report are listed in table 1.

Table 1

Values of Thermodynamic Parameters for $CS_2$†

| State Function | $-72^oC$ | $125^oC$ | $20^oC$ |
|---|---|---|---|
| V ($cm^3/g$) | 0.7163 | 0.9293 | 0.7918 |
| alpha ($^oK^{-1}$) | $1.0317 \times 10^{-3}$ | $1.9803 \times 10^{-3}$ | $1.218 \times 10^{-3}$ |
| $K_T$ (Mbar) | .0211 | .0025 | .0108 |
| $C_p$ (Mbar $cm^3 g^{-1} {}^oK^{-1}$) | $0.989 \times 10^{-5}$ | $1.01 \times 10^{-5}$ | $1.00 \times 10^{-5}$ |

† These values are from references 22 - 26. Note: the $125^oC$ values were extrapolated beyond known data.

# SECTION 5

## ANALYSIS OF RESULTS

### 5.1 ANALYSIS

In tables 2, 3, and 4, I have compiled the P, T, and $\Delta\lambda$ data from the heated, cooled, and room temperature experiments described in section 3. The values listed are interpolations to convenient values of pressure and temperature, taken from the curves for $\Delta\lambda$ -vs- P and T -vs- P. (These interpolations were obtained graphically and may differ slightly from values calculated with the equations fit to the $\Delta\lambda$ -vs- P and T -vs- P data, shown in figures 11 and 14.)

Table 2

Cold SWL (Shot 83-031)

| P(kbar) | $\Delta\lambda(\text{Å})$ | $T(^{\circ}K)$ |
|---|---|---|
| | $(\lambda_o = 3521\text{Å})$ | |
| 0 | 0 | 201 |
| 10 | 162 | 302 |
| 20 | 324 | 358 |
| 30 | 480 | 398 |
| 40 | 644 | 432 |
| 50 | 804 | 459 |
| 9.8 | 158 | 300 |
| 30.5 | 488 | 400 |
| 46.3 | 744 | 450 |

Table 3

Room-Temperature SWL

| P(kbar) | $\Delta\lambda(\text{Å})$ | $T(^{\circ}K)$ |
|---|---|---|
| | $(\lambda_o = 3550\text{Å})$ | |
| 0 | 0 | 293 |
| 10 | 240 | 441 |
| 20 | 438 | 512 |
| 30 | 627 | 561 |
| 40 | 807 | 597 |
| 50 | 976 | 628 |
| 60 | 1142 | 656 |
| 70 | 1373 | 679 |
| 0.3 | 7 | 300 |
| 7.1 | 175 | 400 |
| 18.0 | 398 | 500 |
| 40.8 | 821 | 600 |
| 57.7 | 1095 | 650 |
| 70.5 | 1384 | 680 |

Table 4

Hot SWL  (Shot (83-022)

| P(kbar) | $\Delta\lambda$(Å) | $T(^{\circ}K)$ |
|---------|---------------------|----------------|
|         | ($\lambda_o$=3598Å) |                |
| 0       | 0                   | 398            |
| 10      | 345                 | 586            |
| 20      | 603                 | 644            |
| 30      | 790                 | 681            |
| 40      | 951                 | 709            |
| 50      | 1121                | 731            |
| .05     | 2                   | 400            |
| 3.0     | 126                 | 500            |
| 11.9    | 396                 | 600            |
| 21.3    | 627                 | 650            |
| 29.7    | 784                 | 680            |
| 36.5    | 895                 | 700            |

From the upper part of each table, $\Delta\lambda/\Delta T$ can be calculated at convenient pressures, and from the lower part $\Delta\lambda/\Delta P$ is obtained at convenient temperatures.  For example, $\Delta\lambda/\Delta T$ at 10 kbar, between cold and room-temperature experiments:

Cold experiment : $\lambda = \Delta\lambda + \lambda_0 = 162$Å $+ 3521$Å $= 3683$Å

Room-temp. exp. : $\lambda = \Delta\lambda + \lambda_0 = 240$Å $+ 3550$Å $= 3790$Å

$$\frac{\Delta\lambda}{\Delta T}\bigg]_{10} = \frac{3790 - 3683}{441 - 302} = \frac{107\text{Å}}{139^{\circ}K} = 0.77 \text{ Å}/^{\circ}K$$

Thus, we can construct tables 5 & 6. The data from these tables are plotted in figures 19 through 22.

Table 5 : $\Delta\lambda/\Delta T$

Between Cold & Room Temperature Experiments

| P(kbar) | $\Delta\lambda/\Delta T$ ($\text{\AA}/^\circ K$) | T,avg.($^\circ K$) |
|---------|------------------------|----------|
| 10 | 0.77 | 372 |
| 20 | 0.93 | 435 |
| 30 | 1.08 | 480 |
| 40 | 1.16 | 514 |
| 50 | 1.19 | 543 |

Between Hot & Room-Temperature Experiments

| | | |
|---------|------|-----|
| 10 | 1.06 | 514 |
| 20 | 1.61 | 578 |
| 30 | 1.76 | 621 |
| 40 | 1.71 | 653 |
| 50 | 1.87 | 679 |

Between Cold & Hot Experiments

| | | |
|---------|------|-----|
| 10 | 0.92 | 444 |
| 20 | 1.24 | 501 |
| 30 | 1.37 | 540 |
| 40 | 1.39 | 570 |
| 50 | 1.45 | 595 |

Table 6 : $\Delta\lambda/\Delta P$

Between Cold & Room-Temperature Experiments

| T ($^oK$) | $\Delta\lambda/\Delta P$ ($\overset{\circ}{A}/kbar$) | P,avg.(kbar) |
|---|---|---|
| 300 | 12.8 | 4.9 |
| 400 | 12.1 | 18.8 |
| 450 | 12.9 | 28.7 |

Between Hot & Room-Temperature Experiments

| 400 | 17.7 | 3.5 |
| 500 | 14.9 | 10.5 |
| 600 | 13.0 | 26.4 |
| 650 | 11.5 | 39.5 |
| 680 | 13.5 | 50.1 |

Between Cold & Hot Experiments

| 400 | 13.4 | 15.3 |
| 450 | 12.1 | 23.8 |

## $\Delta\lambda$ / $\Delta T$ :

From figure 19, $\Delta\lambda/\Delta T$ shows an apparently linear increase with temperature, and is fit by the line:

$$\frac{\Delta\lambda}{\Delta T} = 0.415 + 0.003747(T - 300^oK)$$

as shown in the figure. The graph against pressure (figure 20) does not show any clear pressure dependence, but the temperature dependence is apparent.

## $\Delta\lambda$ / $\Delta P$ :

$\Delta\lambda/\Delta P$ is plotted against temperature and pressure in figures 21 and 22 respectively. Neither plot shows any clear dependence on the abscissa.
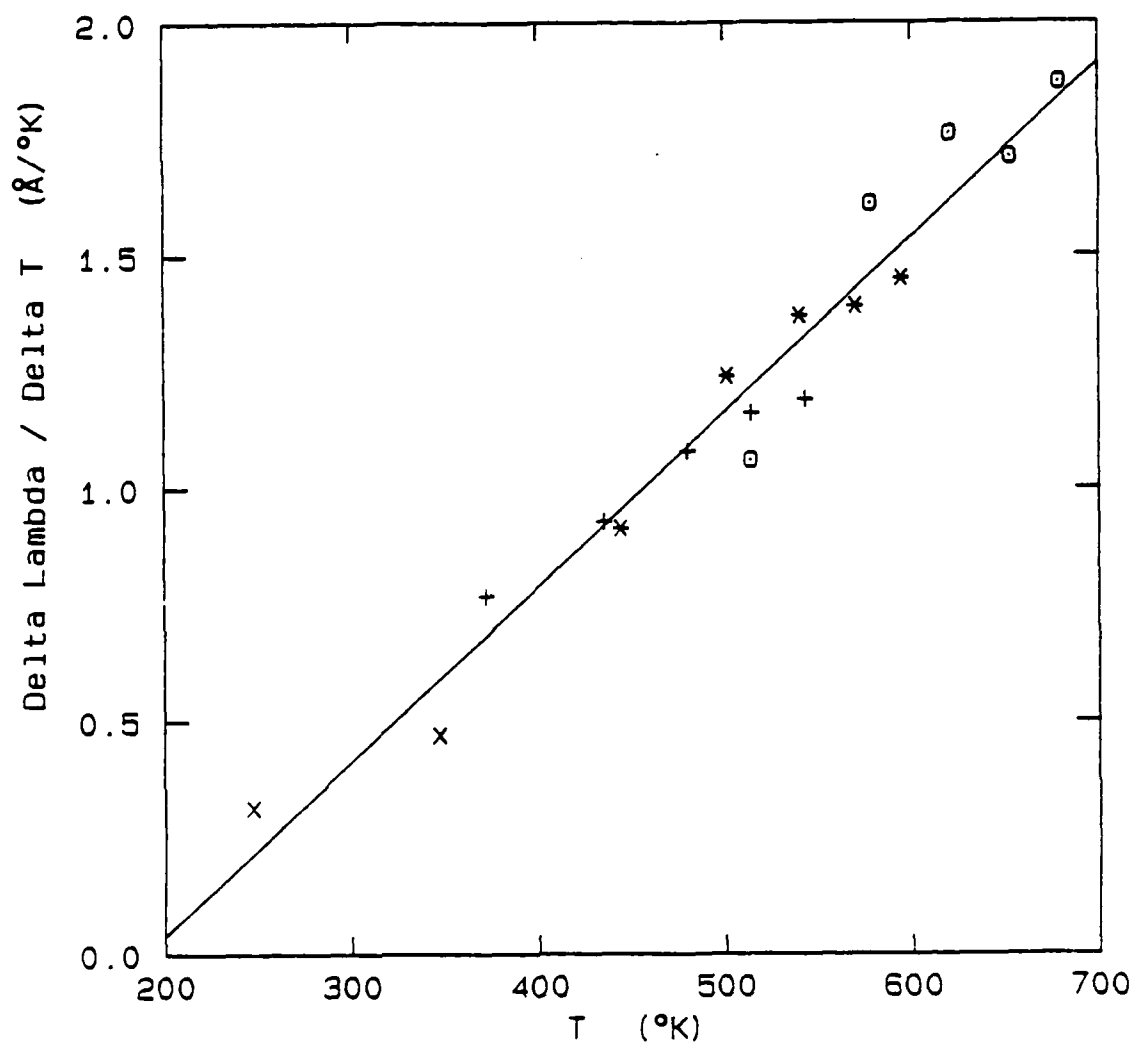
**Figure 19:** $\Delta\lambda/\Delta T$ -vs- T

    X - static data (sec. 3.2)

    + - between cold and room-temperature experiments

    ✱ - between cold and hot experiments

    ☉ - between room-temperature and hot experiments

The line is a least squares fit of all the data and has the equation:

$$\frac{\Delta\lambda}{\Delta T} = 0.415 + 0.003747(T - 300^{\circ}K)$$

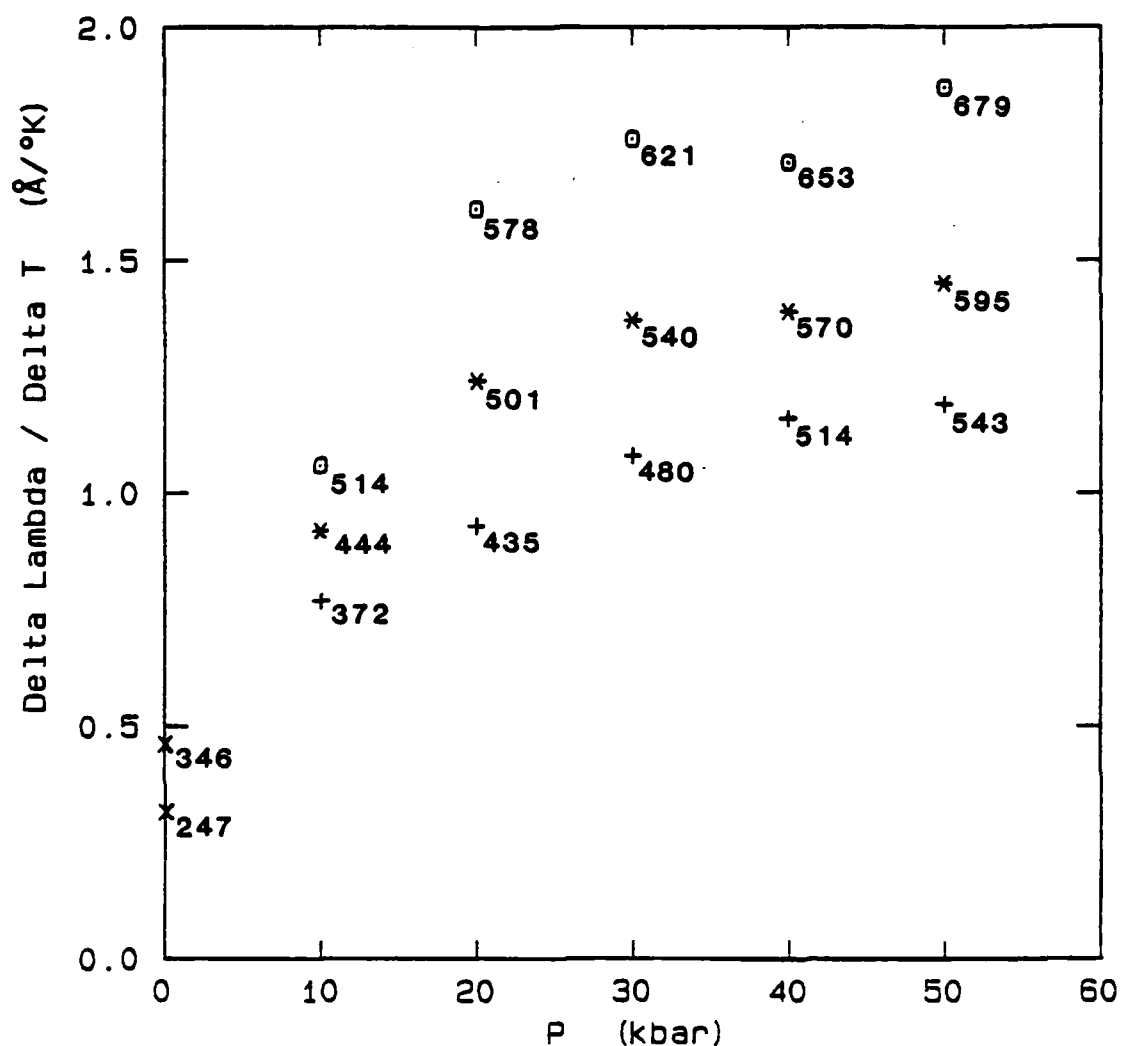where $\Delta\lambda/\Delta T \equiv \mathring{A}/^{\circ}K$.

Figure 20: $\Delta\lambda/\Delta T$ -vs- P

 X - static data (sec. 3.2)

 + - between cold and room-temperature experiments

 ✳ - between cold and hot experiments

 ⊙ - between room-temperature and hot experiments

The number next to each point is the average temperature in $^\circ K$ for that point (from table 5).

Figure 21: $\Delta\lambda/\Delta P$ -vs- T

    + - between cold and room-temperature experiments

    ✳ - between cold and hot experiments
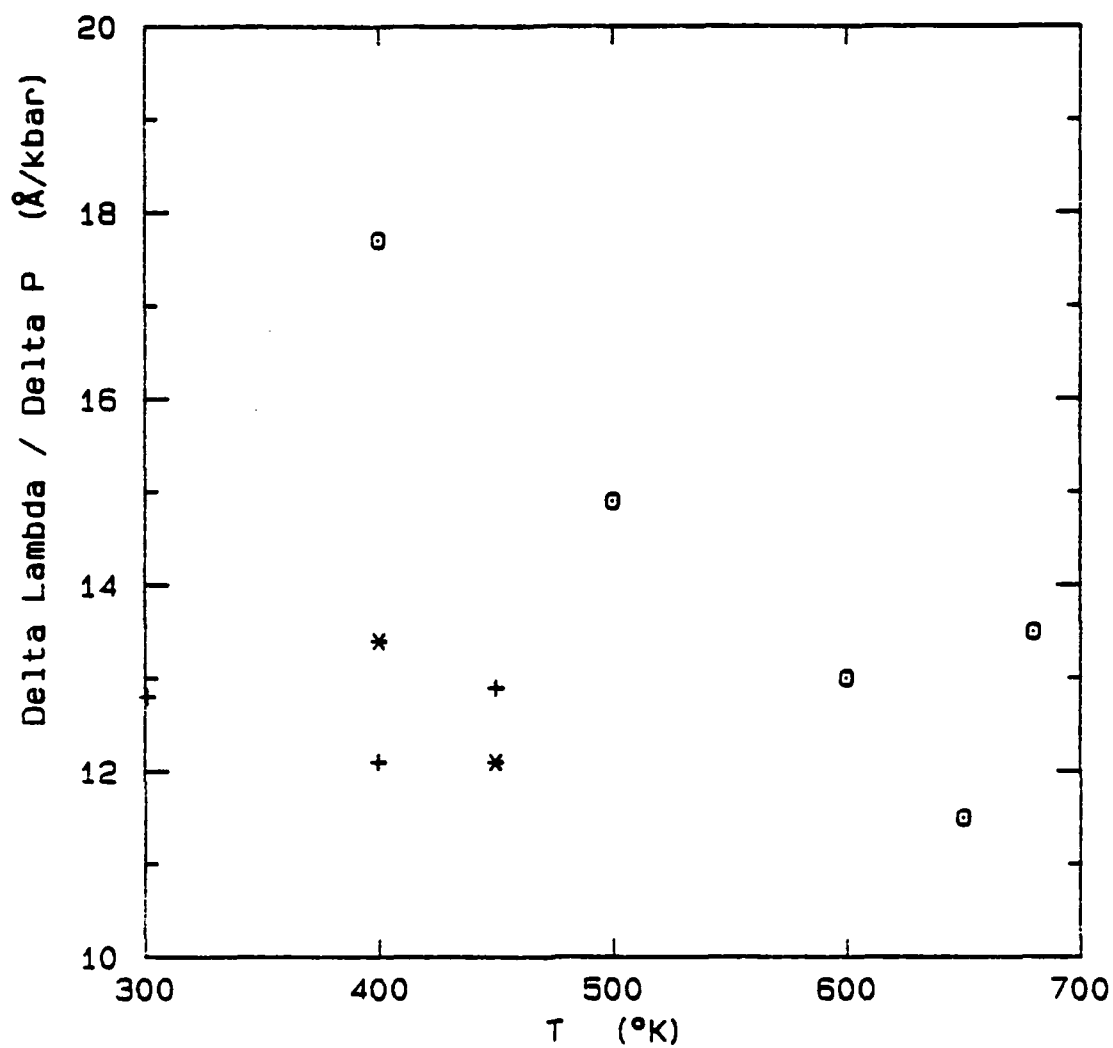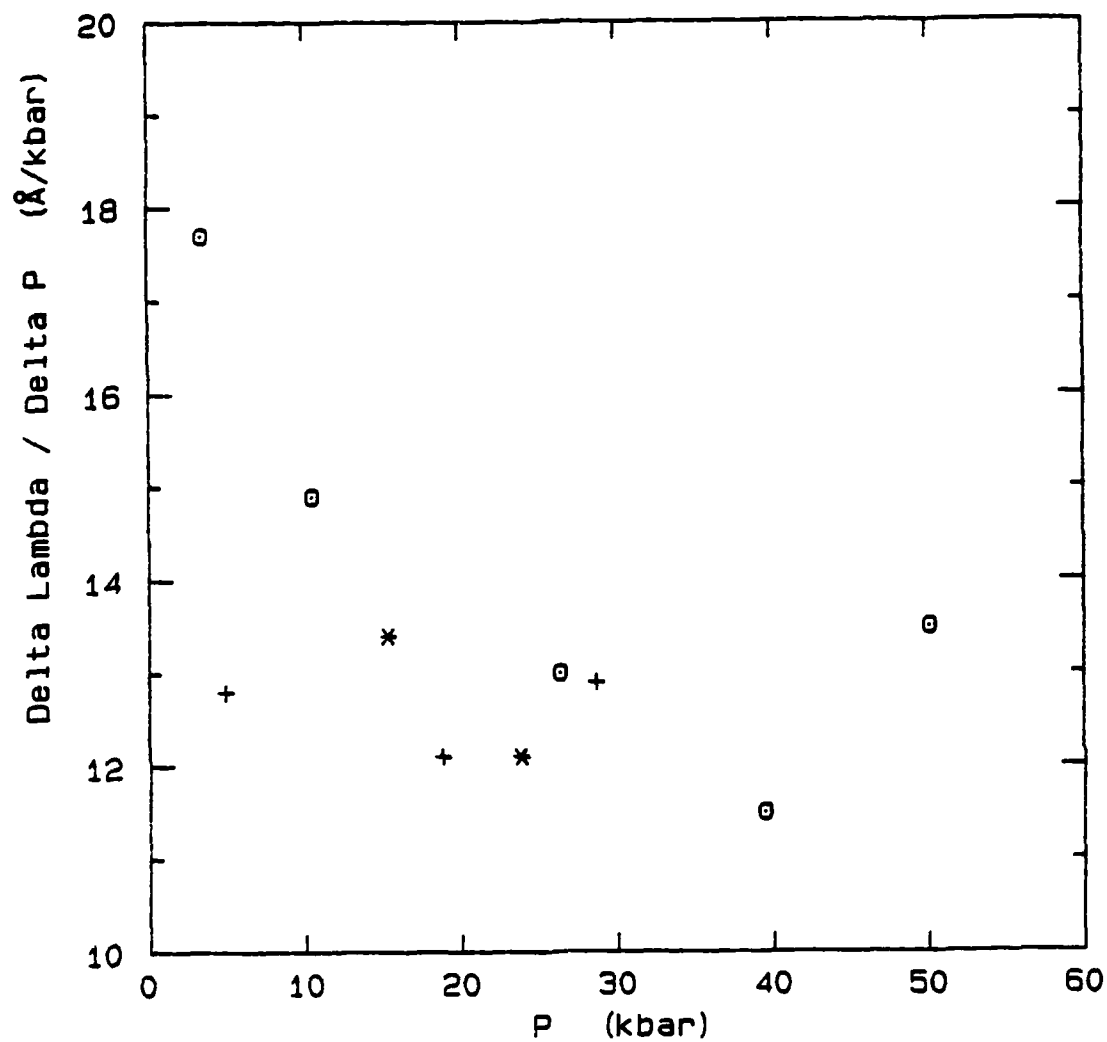
    ⊙ - between room-temperature and hot experiments

Figure 22: $\Delta\lambda/\Delta P$ -vs- P
+ - between cold and room-temperature experiments
✱ - between cold and hot experiments
⊙ - between room-temperature and hot experiments

$\partial\lambda/\partial T$ and $\partial\lambda/\partial P$ :

If we assume that $\partial\lambda/\partial T$ is given by the line drawn in figure 19, then we can calculate $\partial\lambda/\partial P$ for each experiment as follows:

$$d\lambda = \left[\frac{\partial\lambda}{\partial T}\right]_P dT + \left[\frac{\partial\lambda}{\partial P}\right]_T dP \quad (assume \ \lambda = \lambda(T,P))$$

$$\left[\frac{\partial\lambda}{\partial P}\right]_T = \frac{d\lambda}{dP} - \left[\frac{\partial\lambda}{\partial T}\right]_P \frac{dT}{dP}$$

For example, $\Delta\lambda$ -vs- P for shot 83-031 (cold SWL) is plotted as curve C in figure 14. The tangent at any point along the curve gives $d\lambda/dP$. From figure 19, $\partial\lambda/\partial T = 0.415 + 0.003747(T - 300^{\circ}K)$, and dT/dP is the slope of the tangent to the T -vs- P curve in figure 11. Thus we can calculate $\partial\lambda/\partial P$ for any pressure in an experiment. The values of $\partial\lambda/\partial P$ calculated at 10 kbar intervals for the hot, cold, and room-temperature experiments are plotted against temperature and pressure in figures 23 and 24 respectively. $\partial\lambda/\partial P$ displays no dependence on either temperature or pressure. The average value for $\partial\lambda/\partial P$ is 13.4 $\mathring{A}/kbar$.

**Self-Consistency Test :**

The above values for $\partial\lambda/\partial T$ and $\partial\lambda/\partial P$ are applied to each experiment to try and reproduce the $\Delta\lambda$ -vs- P data by using the following relationship:

$$\Delta\lambda = \frac{\partial\lambda}{\partial T}\Delta T + \frac{\partial\lambda}{\partial P}\Delta P$$

The results of this test are listed in table 7. A slightly better overall fit is obtained with a value of 12.8 $\mathring{A}/kbar$ for $\partial\lambda/\partial P$.

**Figure 23:** $\partial\lambda/\partial P$ -vs- T

    + - cooled cell experiment (shot 83-031)

    ✱ - room temperature experiment (shot 82-037)

    ⊙ - heated cell experiment (shot 83-022)

$\partial\lambda/\partial P$ was calculated from: $\quad \dfrac{\partial\lambda}{\partial P} = \dfrac{d\lambda}{dP} - \dfrac{\partial\lambda}{\partial T}\dfrac{dT}{dP}$

where $\partial\lambda/\partial T = 0.415 + .003747(T - 300°K)$ (from fig. 19), and dT/dP and d$\lambda$/dP are from figures 11 and 14 respectively. $\lambda$ is in angstroms, P is in kilobars, and T is in Kelvins.
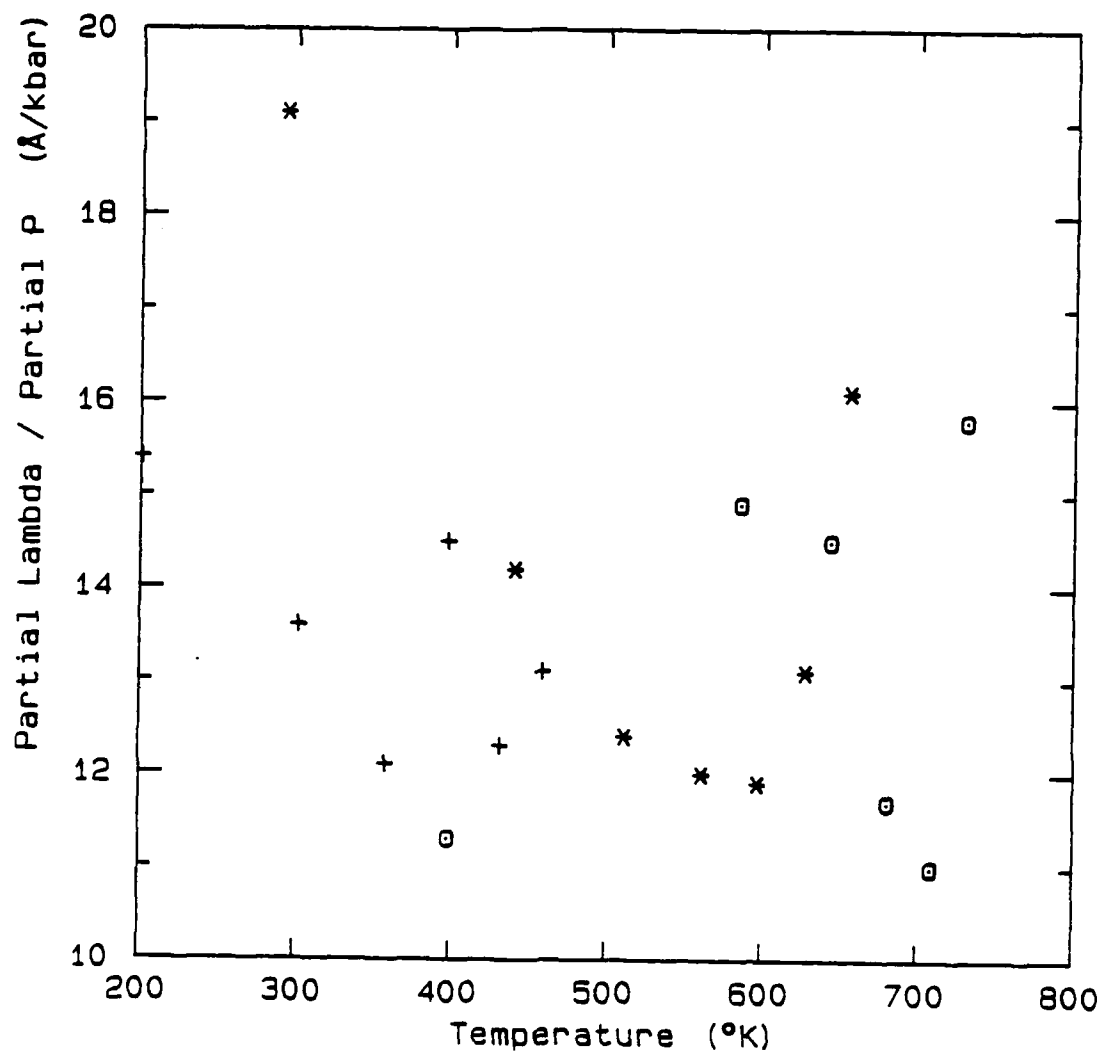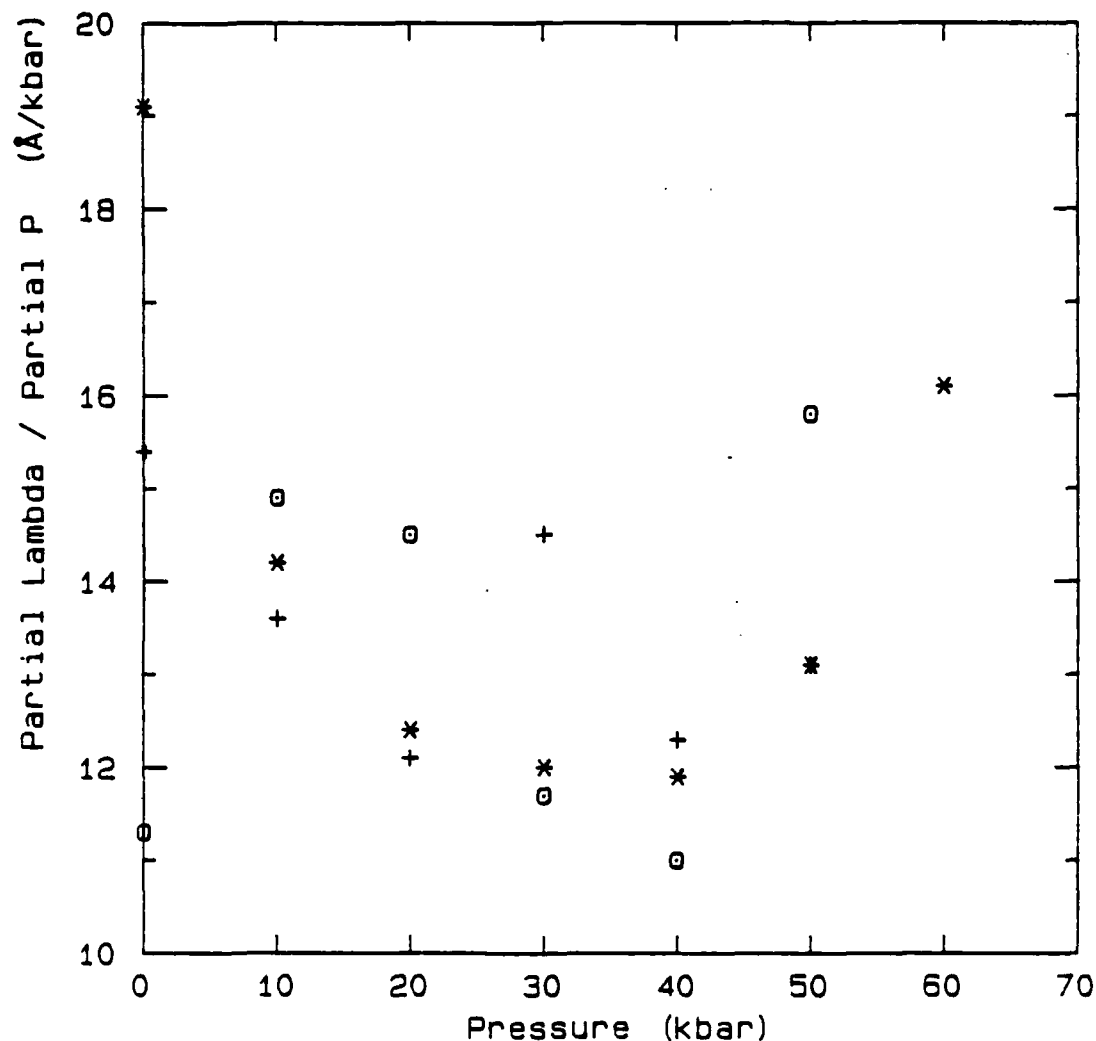
**Figure 24:** $\partial\lambda/\partial P$ -vs- P

    + - cooled cell experiment (shot 83-031)

    ✱ - room temperature experiment (shot 82-037)

    ⊙ - heated cell experiment (shot 83-022)

$\partial\lambda/\partial P$ was calculated from: $\dfrac{\partial\lambda}{\partial P} = \dfrac{d\lambda}{dP} - \dfrac{\partial\lambda}{\partial T}\dfrac{dT}{dP}$

where $\partial\lambda/\partial T = 0.415 + .003747(T - 300^\circ K)$ (from fig. 19), and dT/dP and d$\lambda$/dP are from figures 11 and 14 respectively. $\lambda$ is in angstroms, P is in kilobars, and T is in Kelvins.

Table 7 : Self-Consistency Test: Comparison Of Measured Values of $\Delta\lambda$ (Tables 2-4) With Calculated Values From The Equation:

$$\Delta\lambda = \frac{\partial\lambda}{\partial T}\Delta T + \frac{\partial\lambda}{\partial P}\Delta P$$

with $\partial\lambda/\partial T = 0.415 + .003747(T - 300^{\circ}K)$, and $\partial\lambda/\partial P = 13.4$ ($\lambda$ is in Å, T is in $^{\circ}K$, P is in kbars).

Cold SWL (SHOT 83-031)

| $\Delta P(kbar)$ | $\Delta T(^{\circ}K)$ | $\partial\lambda/\partial P$ (Å/kbar) | $\partial\lambda/\partial T$ (Å/$^{\circ}K$) | $\Delta\lambda$ calculated (Å) | $\Delta\lambda$ actual (Å) | error % |
|---|---|---|---|---|---|---|
| 0-10 | 201-302 | 13.4 | 0.23 | 157.3 | 162 | -2.9 |
| 10-20 | 302-358 | 13.4 | 0.53 | 163.5 | 162 | +0.9 |
| 20-30 | 358-398 | 13.4 | 0.71 | 162.3 | 156 | +4.0 |
| 30-40 | 398-432 | 13.4 | 0.85 | 162.8 | 164 | +0.7 |
| 40-50 | 432-459 | 13.4 | 0.96 | 160.0 | 160 | 0.0 |

Room-Temperature SWL

| | | | | | | |
|---|---|---|---|---|---|---|
| 0-10 | 293-441 | 13.4 | 0.67 | 232.6 | 240 | -3.1 |
| 10-20 | 441-512 | 13.4 | 1.07 | 210.3 | 198 | +6.2 |
| 20-30 | 512-561 | 13.4 | 1.30 | 197.6 | 189 | +4.6 |
| 30-40 | 561-597 | 13.4 | 1.46 | 186.6 | 180 | +3.6 |
| 40-50 | 597-628 | 13.4 | 1.58 | 183.1 | 169 | +8.3 |
| 50-60 | 628-656 | 13.4 | 1.70 | 181.5 | 166 | +9.3 |

Hot SWL (SHOT 83-022)

| | | | | | | |
|---|---|---|---|---|---|---|
| 0-10 | 398-586 | 13.4 | 1.13 | 347.2 | 345 | +0.6 |
| 10-20 | 586-644 | 13.4 | 1.60 | 226.5 | 258 | -12.2 |
| 20-30 | 644-681 | 13.4 | 1.77 | 199.5 | 187 | +6.7 |
| 30-40 | 681-709 | 13.4 | 1.90 | 187.1 | 161 | +16.2 |
| 40-50 | 709-731 | 13.4 | 1.99 | 177.8 | 170 | +4.6 |

## 5.2 UNCERTAINTIES

The pressures and temperatures calculated in this report are based on the Sheffield-II equation of state. The accuracy of this equation to within 2% for shock-pressure calculations has been verified up to 40 kbar.[21] Temperature calculations, however, depend on an assumed function for $C_v$ with shock pressure. Different equations of state can give widely differing results. For example, Lysne and Hardesty[27] have shown that calculated shock temperatures for nitromethane at 200kbar, can differ by nearly a factor of two for different equations of state. The two Sheffield forms (section 4) predict temperatures of $732^\circ K$ and $610^\circ K$ at 50kbar in a SWL experiment. The later Sheffield form, given in reference 20, was used in this report.

There may be unknown errors introduced into the Sheffield equation of state by changing $T_0$. Other uncertainties arise in producing and reading the photographic shot records. The reproducibility in obtaining the pre-shock position of the $CS_2$ band edge in repeat experiments is $\sim\pm15\text{Å}$. In correlating the wavelength shift with the calculated shock pressure, as in figures 9, 13, and 16, small errors in cell thickness measurement can give rise to significant errors in the calculated time-position of the reverberating shock wave.

# SECTION 6
## OTHER MEASUREMENTS

### 6.1 DIAMOND CELL

The 3200Å absorption band in $CS_2$ has been studied in a diamond anvil cell by Agnew & Swanson.[28] They measured the position of the red edge of this band as a function of static pressure at ambient temperature. Their results are plotted in figure 25 along with the shock measurements from this report. For the diamond cell data, $\partial\lambda/\partial P = 9.9$ Å/*kbar*, which is 26% less than the shock data average of 13.4 Å/*kbar*.

### 6.2 NOTE ON REACTION THRESHOLD

Dick[9,10] found a transition to a higher density state in $CS_2$ occurring in single-shock experiments at about 60 kbar. The measurements made in the present report are on "unreacted" $CS_2$, that is, below the temperature and pressure threshold of the transition observed by Dick. In stepwise loading experiments, Duvall, Bellamy, Hegland, Eschbach, and this author showed that an irreversible spectral change occurs in $CS_2$ at 89 kbar.[29] This change appears to be the same transition observed by Dick, but occurs at a higher pressure due to the lower temperature in a multiple-shock compression as opposed to a single-shock compression.
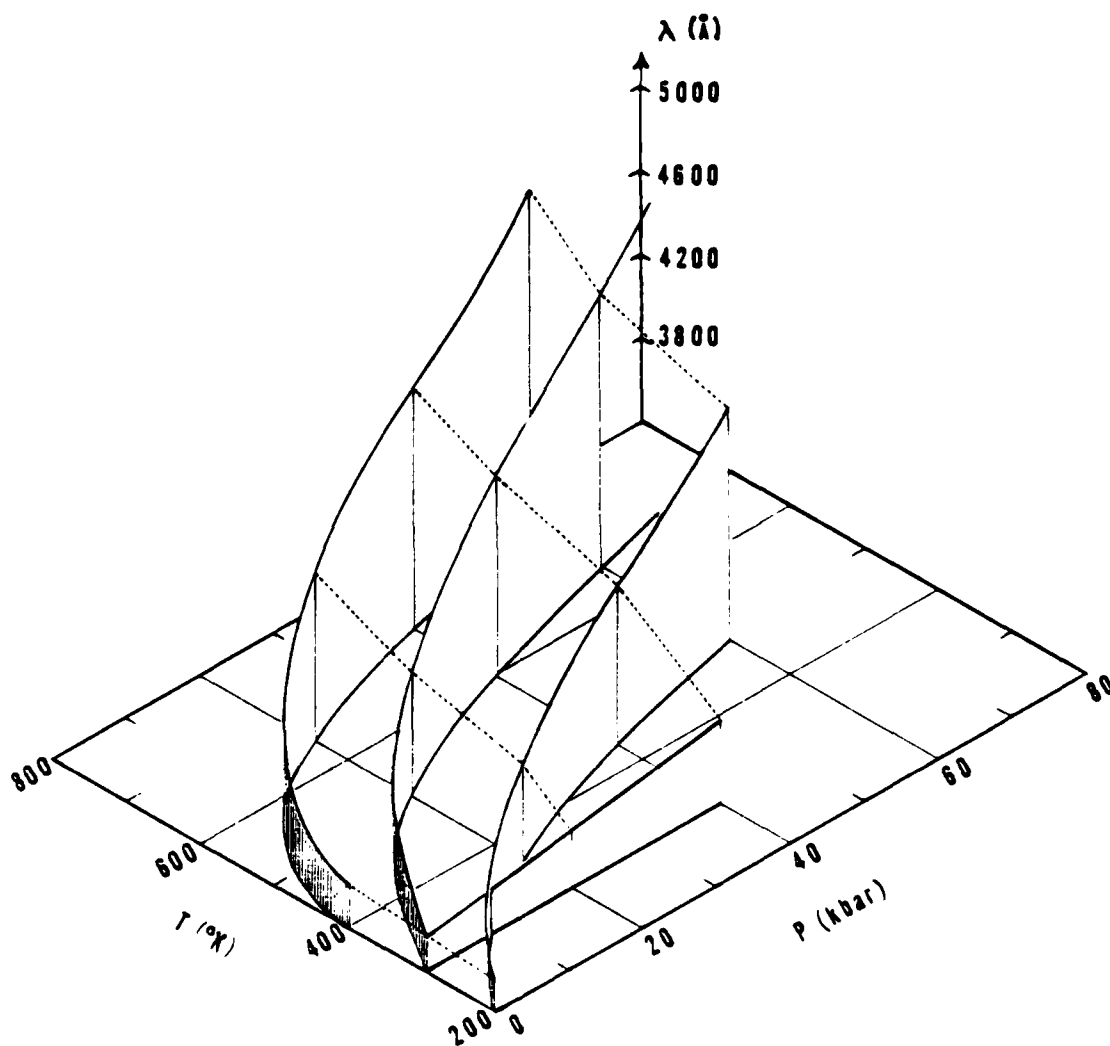
**Figure 25: P-T-λ Surface For Liquid CS₂**

This surface shows the position of the red edge of the 3200Å absorption band in $CS_2$, as a function of pressure and temperature. Three of the curves depicting the surface are the results of shock experiments on $CS_2$ at three different initial temperatures: $201°K$, $293°K$, and $398°K$. The isothermal curve at $293°K$ is the result of diamond anvil cell measurements made by Agnew and Swanson.[28] The dotted lines connect points of constant pressure.
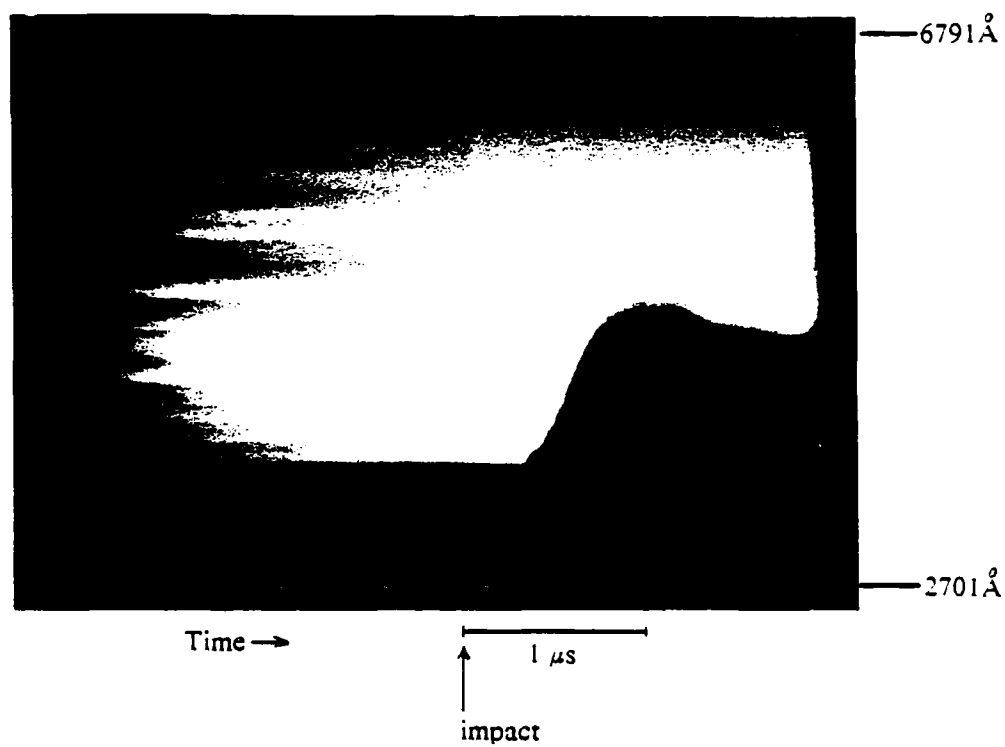
# SECTION 7

## CONCLUSIONS / RECOMMENDATIONS

Heated and cooled spectroscopy cells were successfully employed in shock experiments to record time-resolved spectra of liquid $CS_2$. The red edge of the lowest energy electronic absorption band in liquid $CS_2$ exhibits a highly regular shift that appears to be a function only of pressure and temperature. The temperature component seems independent of pressure, but appears to increase linearly with temperature by $\partial\lambda/\partial T = 0.415 + 0.003747(T - 300°K)$. The pressure component of the shift appears roughly constant at ~13 $Å/kbar$ ±~20%. Static data (diamond cell)[28] indicate a value of 9.9 $Å/kbar$ for isothermal compression at room temperature. Further thermal measurements need to be made on $CS_2$ at high pressures and temperatures in order to remove the uncertainty in the equation of state temperature calculations, and to provide correct thermodynamic values for initial conditions in the experiment at 125°C.

**APPENDIX**

SUMMARY OF EXPERIMENTS

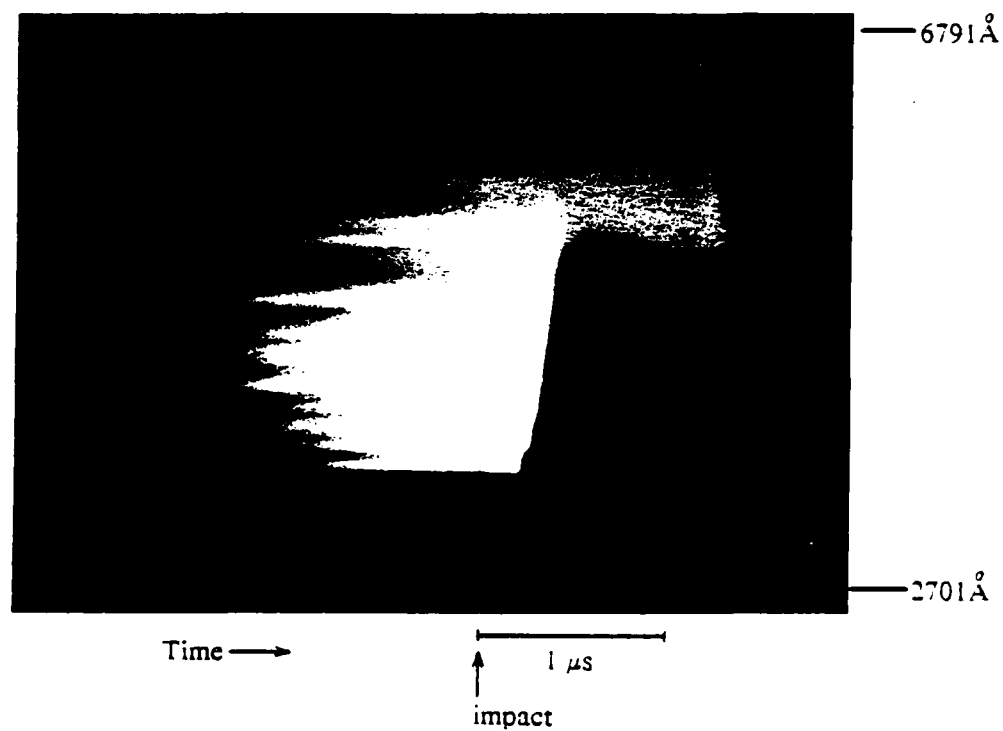| Shot Number | $T_0(^\circ K)$ | Impact Pressure (kbar) | Final T($^\circ K$) | Cell Thickness (microns) |
|---|---|---|---|---|
| 82-031 | 293 | 54 | 617 | 165 |
| 82-028 | 293 | 75 | 683 | 116 |
| 82-037 | 293 | 81 | 701 | 160 |
| 83-014 | 293 | 130 | 844 | 158 |
| 82-015 | 293 | 71 | 670 | 180 |
| 83-022 | 398 | 65 | 757 | 164 |
| 83-031 | 201 | 61 | 486 | 158 |

**PLATE 1**



Time →    |——— 1 μs ———|
          ↑
          impact

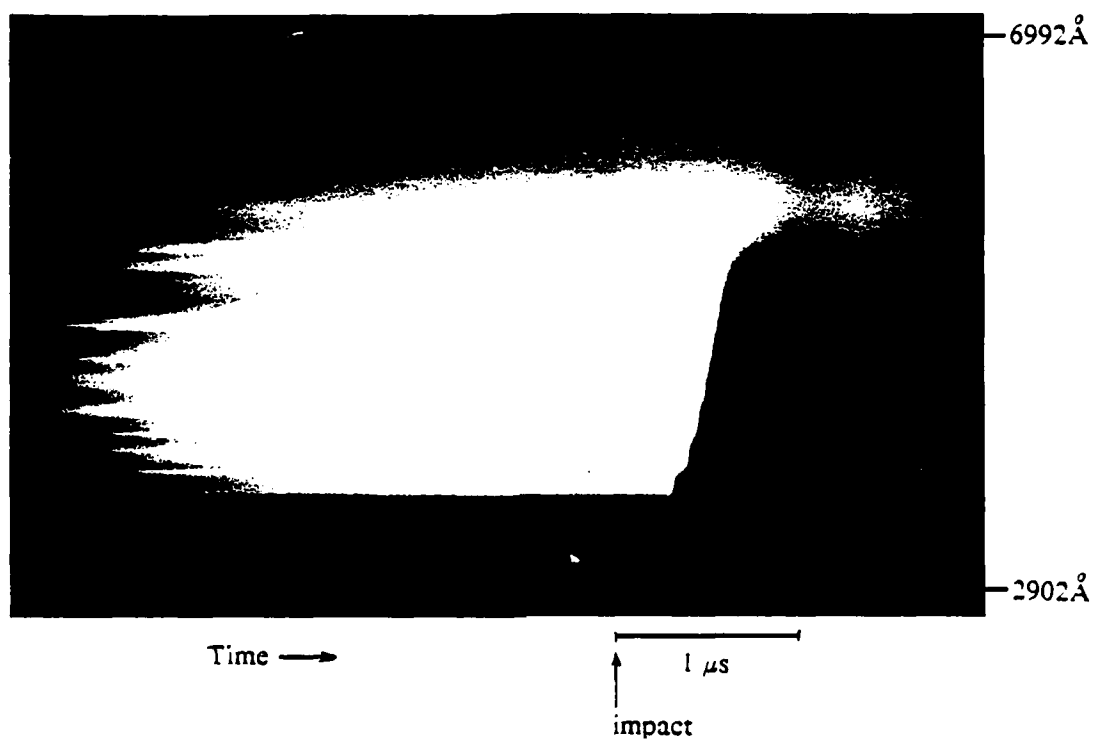6791Å (top right label)
2701Å (bottom right label)

**SHOT 82-031**

**Impact pressure = 54 kbar**
**Cell thickness = 165 microns**

PLATE 2



SHOT 82-028

Impact pressure = 75 kbar
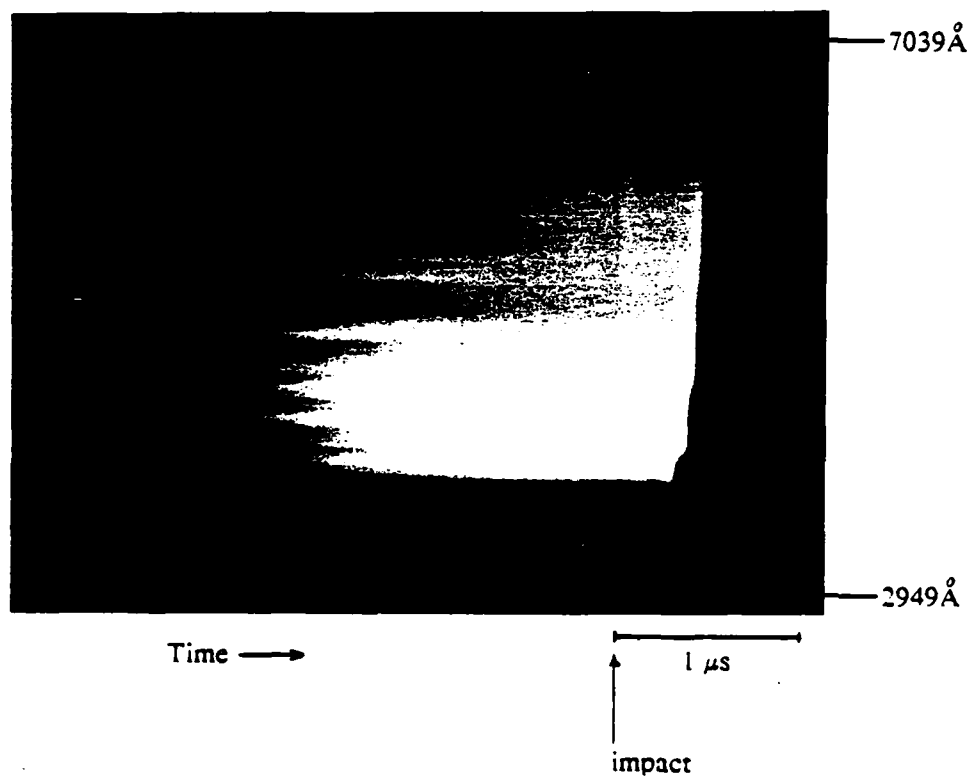Cell thickness = 116 microns

**PLATE 3**



Time ⟶

1 μs

impact

6992Å

2902Å

**SHOT 82-037**

**Impact pressure = 81 kbar**
**Cell thickness = 160 microns**

**PLATE 4**



— 7039Å
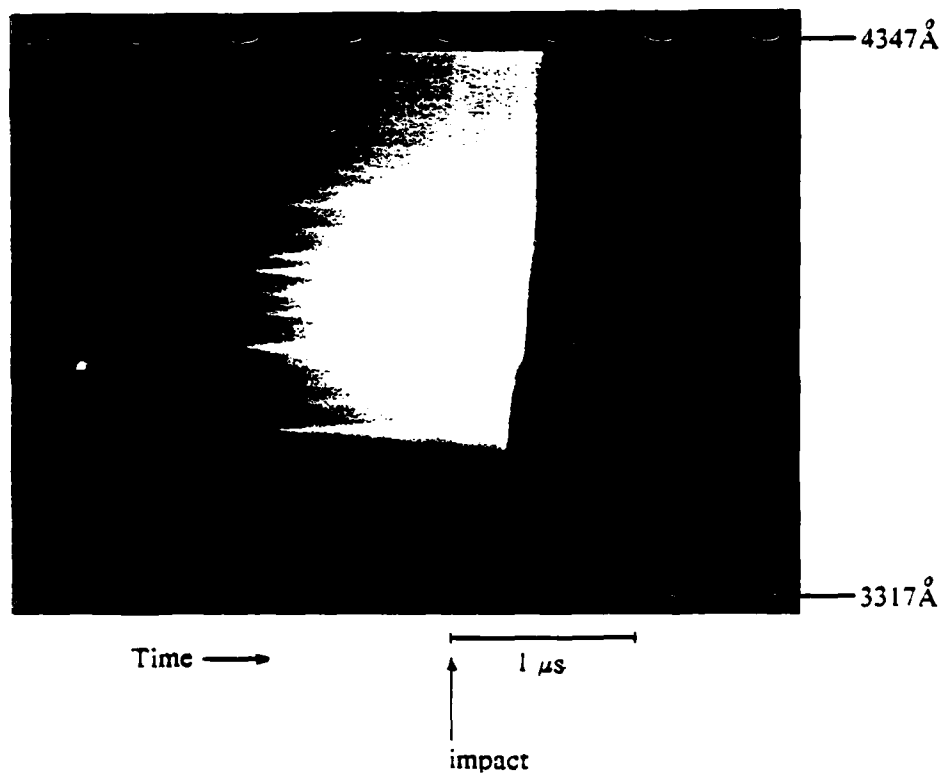
— 2949Å

Time ⟶

⊢——————⊣
1 μs

↑
impact

**SHOT 83-014**

**Impact pressure = 130 kbar**
**Cell thickness = 158 microns**

(Apparent initial absorption band edge is at 3710Å This is higher than the true band edge of 3550Å becq; e in this experiment the light passed through a lucite filter which absorbs up to 3710A

**PLATE 5**


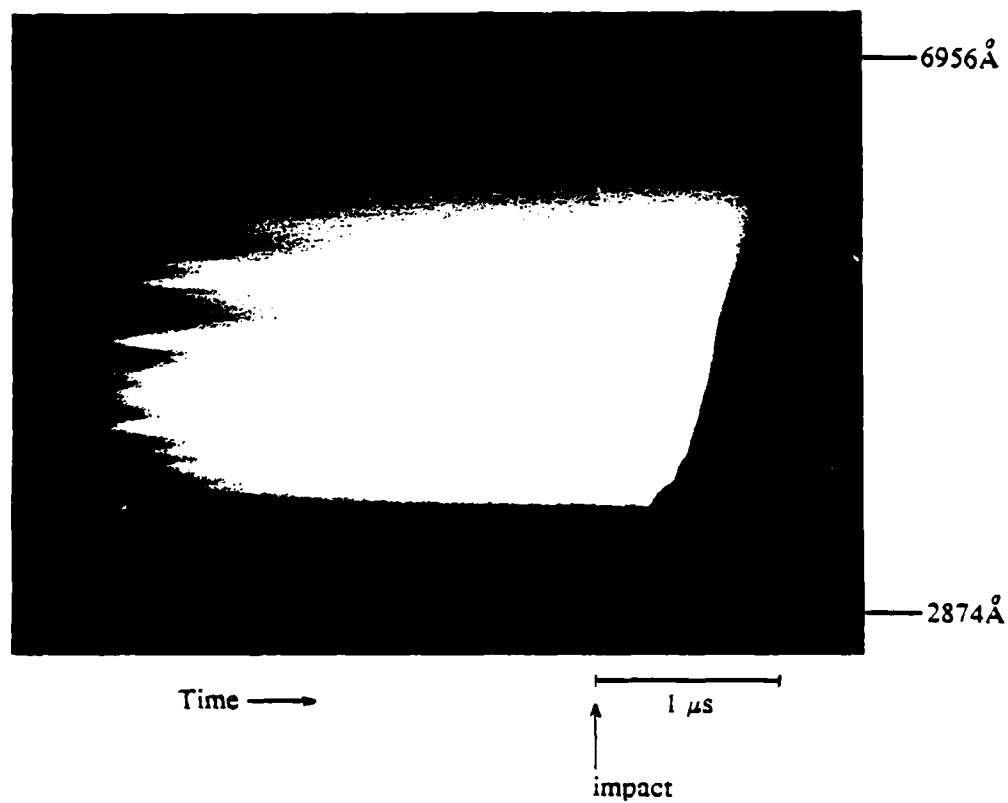
4347Å

3317Å

Time ⟶          |— 1 μs —|

↑
impact

**SHOT 82-015**

**Impact pressure = 71 kbar**
**Cell thickness = 180 microns**
Note: the wavelength scale of this record is expanded 4X.

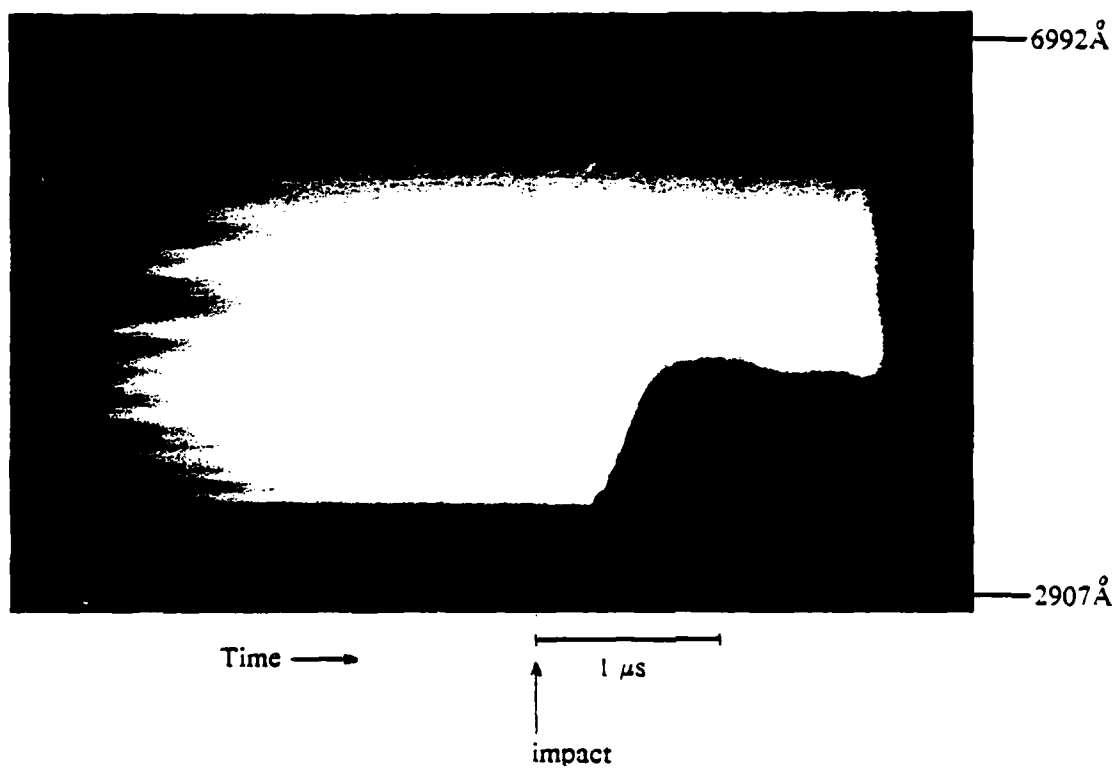**PLATE 6**



SHOT 83-022

Heated cell experiment
Impact pressure = 65 kbar
Cell thickness = 164 microns
$T_0 = 398°K$

PLATE 7



6992Å

2907Å

Time ⟶

1 μs

impact

SHOT 83-031

Cooled cell experiment
Impact pressure = 61 kbar
Cell thickness = 158 microns
$T_0 = 201°K$

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